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Pu Immobilization – Induction Melting and Offgas Testing

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REVIEWS AND APPROVALS

AUTHORS:

T.M. Jones, Process Science and Engineering Section Date

J.R. Zamecnik, Process Science and Engineering Section Date

D.H. Miller, Process Science and Engineering Section Date

D.T. Herman, Chemical Science and Technology Section Date

J.C. Marra, Materials Science and Technology Section Date

TECHNICAL REVIEWER:

M.E. Smith, Process Science and Engineering Section Date

APPROVERS:

R.E. Edwards, Manager, Process Science and Engineering Section Date

D. A. Crowley, Manager, Stabilization Science Research Date

D. P. Eisele, NMM Facilities Engineering Customer Date

EXECUTIVE SUMMARY

The Cylindrical Induction Melter (CIM) at the Aiken County Technology Laboratory (ACTL) has been operated by the Savannah River National Laboratory (SRNL) to support the Pu Disposition Conceptual Design (CD-0) development effort.[1]

The primary purpose of this report is to summarize the offgas sampling tests conducted in the CIM to capture and analyze the particulate and vapors emitted from lanthanide borosilicate (LaBS) Frit X with HfO_2 as a surrogate for PuO_2 and added impurities. In addition, this report describes several initial tests of the CIM for the vitrification of LaBS Frit X with HfO_2. The activities required to produce Frit X from batch chemical oxides for subsequent milling to yield glass frit of nominally 20 micron particle size are also discussed.

The tests with impurities added showed that alkali salts such as NaCl and KCl were substantially emitted into the offgas system as the salt particulate, HCl, or Cl_2. Retention of Na and K in the glass were about 80 and 55%, respectively. Chloride retention was about 35%; chloride remaining in the glass was 0.29-0.37 wt%. Based on a material balance, approximately 83% of F fed was retained in the glass at about 0.09 wt % (F could not be measured directly at this concentration). Transition metals (Ni, Cu, Fe, Mo, Cr) were also volatilized to varying extents. A very small amount (<0.1 g) of nickel compounds and KCl were found in crystals deposited on the melter offgas line. Overall, about 58-72% of the impurities added were volatilized. Virtually all of the particulate species were collected on the nominal 0.3 μm filter. The particulate evolution rate ranged from 2-8 g/kg glass/h. The particulate was found to be as small as 0.2 μm and have an approximate median size of 0.5 μm. The particulate salt was also found to stick together by forming bridges between particles.

Further runs without washable salts are recommended. Measurements of particle size distribution for use in offgas system design and tests of simple impingement devices for particle collection are also recommended for tests in the near future.

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LIST OF ACRONYMS

ACTL	Aiken County Technology Laboratory
AD	Analytical Development
CIM	Cylindrical Induction Melter
DF	Decontamination Factor
DOE/EM	Department of Energy Office of Environmental Management
DWPF	Defense Waste Processing Facility
EDS	Energy Dispersive X-Ray Spectroscopy
HLW	High Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectroscopy
LaBS	Lanthanide Borosilicate (glass)
M&TE	Measuring & Test Equipment
Pt/Rh	Platinum/Rhodium
PDP	Plutonium Disposition Project
PIP	Plutonium Immobilization Project
PSAL	Processing Science Analytical Laboratory
scfh	standard cubic feet per hour
SEM/EDS	Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTR	Technical Task Request
VPWF	Vitrified Plutonium Waste Form
WSRC	Washington Savannah River Company

1.0 INTRODUCTION AND BACKGROUND

The Department of Energy-Environmental Management (DOE-EM) plans to conduct the Plutonium Disposition Project (PDP) at the Savannah River Site (SRS). An important part of this project is to reduce the attractiveness of plutonium scrap by fabricating a durable plutonium glass form and immobilizing this Pu form within the high level waste (HLW) glass prepared in the Defense Waste Processing Facility (DWPF). In support of the previous Plutonium Immobilization Program (PIP), a glass formulation was developed that was capable of incorporating large amounts of actinides as well as accommodating any impurities that may be associated with Pu feed streams. The basis for the glass formulation was derived from commercial glasses that had high lanthanide loadings. A development effort[2] led to a Lanthanide BoroSilicate (LaBS) glass that accommodated significant quantities of actinides, tolerated impurities associated with the actinide feed streams and could be processed using established melter technologies. A Cylindrical Induction Melter (CIM) was developed during the PIP for vitrification of the Pu LaBS glass. The CIM system consisted of an inductively heated platinum rhodium (Pt-Rh) containment vessel (3” diameter), an induction heating system, a control system and an offgas filtering system. Following the PIP, the CIM melter was extensively studied and refined in support of the Am/Cm vitrification development program.[3]

Although significant testing has been conducted on the CIM in support of Am-Cm vitrification, the application to vitrification of Pu has not been extensively tested. Experimental studies on the vitrification of plutonium oxide surrogates were begun to support the PDP. In these studies, PuO_2 surrogate (HfO_2) feed streams, some containing various impurities, and LaBS glass frit were fed to the CIM to produce the glass product. Thorough evaluation of melter operating parameters and melter performance for this application are required. Testing of the CIM with impurities that are likely to be present in the Pu feeds is also required to evaluate the effect of the impurities on the glass produced, to quantify the offgases produced during the vitrification process, and to begin the process of testing offgas treatment systems.

2.0 APPROACH

Sixteen vitrification runs were completed in the CIM where LaBS Frit X glass was processed (See Table 1). In the initial three runs, raw batch chemicals were measured and pre-blended prior to processing in the CIM to produce LaBS Frit X glass cullet. The cullet produced in the Runs 1-3 was next milled in ball mill jars to a nominal 140 mesh size to resemble frit. For Runs 4-6, LaBS Frit X (from Runs 1-3) was processed with HfO_2 added to represent 9.5 wt% PuO_2 on a molar basis. The LaBS Frit X cullet from Runs 4-6 was processed in Run 7 to produce glass that was poured into a prototypical stainless steel canister to measure the temperature on the outer surface of the canister as the can and glass cooled. Runs 8-13 processed raw batch chemicals to produce more LaBS Frit X cullet for future melter and offgas tests. The cullet produced by these runs (15 kg) was milled using an attritor mill by an outside contractor to size reduce the cullet to the desired nominal 20 micron grain sized frit. Runs 14-16 processed LaBS Frit X with chemical additions blended with the frit to simulate impurities expected to be present in the PuO_2 powder to be processed by the plant. The purpose of Run 14 (NaCl Run) was to sample the offgas emissions and fumes that are generated during the vitrification of the LaBS Frit X blended with NaCl. Run 15 (Rocky Flats Run) sampled the offgas emitted while vitrifying LaBS Frit X blended with simulated Rocky Flats Can B5495 impurities (see Section 2.4), and Run 16 (Remelt Run) sampled the offgas emitted as the glass produced from Run 15 was reheated to complete the evolution of volatiles.

Table 1 Runs Performed To Process LaBS Frit X Materials

Date	Run Title	Material Processed in CIM
6/29/06	Run 1 Process Frit X Batch To Produce Cullet	2170 g Frit X Batch Chemicals
7/11/06	Run 2 Process Frit X Batch To Produce Cullet	2193 g Frit X Batch Chemicals
7/13/06	Run 3 Process Frit X Batch To Produce Cullet	3264 g Frit X Batch Chemicals
8/9/06	Run 4 Frit X With HfO2 Sub for 9.5 wt% PuO2	1849.2 g Frit X (140 mesh) with 150.8 g HfO2 blended in
8/1606	Run 5 Frit X With HfO2 Sub for 9.5 wt% PuO2	1849.2 g Frit X (140 mesh) with 150.8 g HfO2 blended in
8/17/06	Run 6 Frit X With HfO2 Sub for 9.5 wt% PuO2	1849.2 g Frit X (140 mesh) with 150.8 g HfO2 blended in
8/24/06	Run 7 Fill Canister With LaBS Frit X Glass	6020 g LaBS Frit X cullet from Runs 4, 5 and 6
9/5/06	Run 8 Process Frit X Batch To Produce Cullet	3000 g Frit X Batch Chemicals
9/6/06	Run 9 Process Frit X Batch To Produce Cullet	3100 g Frit X Batch Chemicals
9/7/06	Run 10 Process Frit X Batch To Produce Cullet	2600 g Frit X Batch Chemicals
9/13/06	Run 11 Process Frit X Batch To Produce Cullet	2600 g Frit X Batch Chemicals
9/18/06	Run 12 Process Frit X Batch To Produce Cullet	3189 g Frit X Batch Chemicals
9/20/06	Run 13 Process Frit X Batch To Produce Cullet	3191 g Frit X Batch Chemicals
10/11/06	Run 14 Process Frit X with NaCl Impurity Addition aka “NaCl Run” or “Run 101006”	~3000 g Frit X / HfO2 / NaCl blend
10/26/06	Run 15 Process Frit X with Rocky Flats B5495 Addition aka “Rocky Flats Run” or “Run 102606”)	2981 g Frit X / HfO2 / Rocky Flats Can B5495 surrogate blend
11/1/06	Run 16 Reprocess Run 15 Cullet Product aka “Remelt Run” or “Run 110106”	2833 g glass from Run 15

2.1 Preparations for Testing

A number of preparations were required to be completed before initiation of LaBS glass melter testing. These activities included: procurement of chemicals, batching of LaBS frit, fabrication of LaBS frit, and readying the CIM for testing.

2.1.1 Chemical Procurement and Frit Fabrication

An inventory of available chemicals was made and chemicals were ordered. It should be noted that hafnium oxide (HfO_2) was used as a surrogate for plutonium oxide (PuO_2). As is standard practice when substituting for a radioactive element in glass, the hafnium was substituted for the plutonium on a equimolar basis. Therefore, the weight percent of HfO_2 in the glass will not equal the weight percent of PuO_2 in a comparable radioactive glass.

Batch sheets were prepared to specify the chemicals and quantities needed to prepare the frit batch. The chemicals were batched in accordance with these batch sheets. The batch sheets were posted in the laboratory notebooks WSRC-NB-2001-00086 [4]and WSRC-NB-2006-00144[5].

The glass frit was fabricated using the CIM. The batch chemicals were added into the CIM and melted. The discharged glass was “fritted” by pouring it from the melter into water. The resulting glass cullet was dried before sizing for final simulant Pu batch preparation. The composition of the fabricated cullet was verified via chemical analysis in the SRNL Mobile Lab before use in subsequent melter testing. The cullet was initially size reduced using a ball mill to provide nominally -140 mesh (-106 micron) sized frit feed for the melter. Subsequent cullet produced in the CIM to support offgas impurities tests was milled by an outside vendor utilizing an attritor mill to attain 20 micron sized frit.

2.1.2 Surrogate Pu Vitrification Testing in the CIM

The CIM was prepared to support the LaBS glass pour testing. A photo of the CIM at ACTL is shown in Figure 1. For the CIM to be in proper working order, the calibration of process thermocouples had to be performed to ensure that the melting process is prototypical. The CIM also had to be capable of maintaining the glass melt at a temperature of 1500°C for 4 hours, then draining the glass product into an appropriate receipt container.

In advance of design and installation of an offgas filtering system, melter testing was conducted in the CIM using an existing fume hood configuration and glass compositions that contained no impurities (i.e. no hazardous species). These tests provided initial data regarding melter operating performance and throughput. Melter feed was batched using LaBS Frit X and HfO_2 as a surrogate for PuO_2 on an equivalent molar basis. Specific objectives of these tests included evaluation of dry feed (powder) melting behavior, melter operation parameters (power input and temperature), melter pouring behavior, melter cycle time, melter structural behavior, and glass quality produced by the test runs.

Batch sheets were prepared to specify the quantities of frit, hafnium oxide and other additives to be blended to produce the glass batch. The Frit X and HfO_2 were batched in accordance with these batch sheets, which were affixed into the laboratory notebooks, WSRC-NB-2001-00086 and WSRC-NB-2006-00144.

Individual run plans were developed for each melter campaign. The run plans specify the specific objectives for each campaign and identify specific test criteria to measure during the test campaign. The run plans and data associated with the campaign are included in the laboratory notebooks, WSRC-NB-2001-00086 and WSRC-NB-2006-00144.

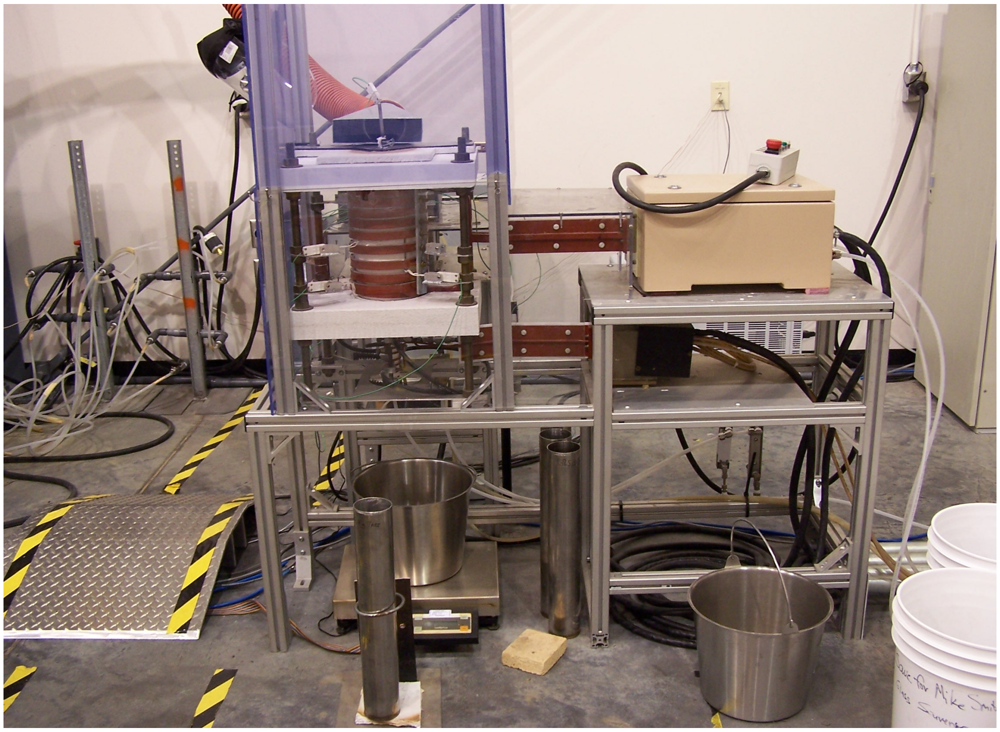


Figure 1 Cylindrical Induction Melter

2.1.3 Offgas System Design, Procurement and Installation for Impurities Testing

Some form an of offgas system will be required for operating the CIM with Pu in a glovebox environment. The specific requirements of the offgas system are not known at this time. This subtask evaluated likely requirements for the offgas system in order to provide information to support the design of a suitable offgas system. An offgas sampling system was coupled with the CIM for testing with impurity compositions.

Offgas systems had been previously designed for the CIM for applications in the PIP and Am/Cm vitrification efforts. The system designed for PIP was never fabricated or tested. The PIP offgas system design will be evaluated for applicability to facilitate design for the current application. The requirements for the Am/Cm system were different because the Am/Cm flowsheet utilized a liquid feed to the melter. However, the design for the Am/Cm vitrification system may also provide insight into design aspects for the current dry-feed application.

2.1.4 Impurity Testing at Crucible Scale

Impurity testing was conducted at the crucible and smaller scale to provide a basis for the melter scale testing. This work examined the effects of several likely impurities on the glass produced and also estimated the volatility of the impurity species by thermogravimetric analysis. The results of these tests have been documented in a separate report.[6]

2.1.5 Impurity Feed Melter Testing

The melter coupled with the offgas sampling system was utilized for impurity feed testing to demonstrate processing of the impurity feed compositions and identify any challenges associated with specific feeds by analysis of the particulate and fume samples collected. Due to the time requirements associated with this task, only very limited impurity feed testing was completed in this initial phase of testing. It is anticipated that extensive follow-on testing will be conducted in a future task.

Melter feed was batched using LaBS Frit X frit, HfO_2 as a surrogate for PuO_2 on an equivalent molar basis, and impurity components anticipated for the various feed streams. Specific objectives of this testing included evaluation of: melter operation parameters, offgas behavior, melter structural behavior, and glass quality produced from the impurity feeds tested.

Batch sheets were prepared to specify the quantities of frit, hafnium oxide and impurities needed to prepare the glass batch. The frit, HfO_2 and impurities were batched in accordance with these batch sheets, and the batch sheets were included in the laboratory notebooks.

A run plan was developed for each melter campaign that specified objectives for the campaign and identified test criteria to measure during the test campaign. The run plans and data associated with the campaign were included in the laboratory notebooks.

2.2 Cylindrical Induction Melter Testing Details

2.2.1 LaBS Frit X Batch Preparation

2.2.1.1 Batch Chemicals Preparation and Processing

The basic LaBS Frit X batch used for the CIM runs was produced from raw batch chemical oxides. The nominal LaBS Frit X batch composition is shown in Table 2. After each constituent was weighed to comprise a nominal 2 kg final glass product, the total quantity of materials was blended together in a ball mill to achieve intimate mixing. The blended batch was then heated to 1400°C in the CIM, where it was homogenized for three hours by air bubbling prior to draining into water to yield cullet.

Table 2 Nominal LaBS Frit X Batch Composition

Oxide	Mass %
Al_2O_3	10.00
B_2O_3	13.00
Gd_2O_3	13.50
HfO_2	7.00
La_2O_3	19.00
Nd_2O_3	15.00
SiO_2	20.00
SrO	2.50
Total	**100.00**

2.2.1.2 Cullet Size Reduction

The cullet produced by Runs 1-3 was ball milled to a nominal 140 mesh size. 500 g quantities of cullet were ball milled for 2 hours, then sieved with a 30 mesh screen. The material that passed through the 30 mesh screen was bagged as feed stock for the melter. The material larger than 30 mesh was returned to the ball mill with additional un-milled cullet to make up the balance of 500 g, and milled for 2 hours. This process was repeated until all of the available cullet was milled sufficiently to pass through the 30 mesh sieve. The particle size distribution of a sample of the milled material is shown in Table 3.

Table 3 Ball Milled LaBS Frit X Sieve Analysis

Sieve Size Mesh	% Retained
50	9.29
140	51.23
200	19.46
325	15.42
400	2.58
635	1.31
Total	**99.29**

2.2.2 Melter Process Testing - Process Batch Chemicals to Produce Frit X Cullet

Nominally 2 to 3 kg of batch chemical oxides were charged to the empty CIM melter vessel. A 2000 g charge of batch chemicals resulted in a batch bed height of 7 inches inside the 14 inch tall CIM vessel, and 3 kg of batch chemicals measured 10 inches. (The batch materials and bed heights for the CIM tests are shown in Table 4.) Then, the vessel cylinder and conical bottom induction heaters were energized at the minimum induction power (0/4095) for 30 minutes to ensure that any moisture present within the batch was driven off. (Note: 0/4095 indicates the controller output used. The output can be set to any integer value from 0 to 4095.)

Additional heating time at minimum induction power input was required when more than 2 kg of batch chemicals were being processed in the CIM to allow chemically bound water (from the boric acid in the batch) to be driven from the batch bed. Heating larger charges of batch too quickly may cause a significant batch bed expansion as the chemically bound water diffuses through the powders to escape. When a bed expansion occurs, the mass of batch chemicals rises up within the CIM vessel. Continued bed expansion could eventually contact the top insulation cover and in severe cases could spill over onto the top of the CIM upper insulation block.

The emission of the moisture from the batch bed entrained a small amount of batch powder as it vented from the top of the CIM vessel and into the offgas air sweep. This emission of batch solids was not as evident when frit was being processed, probably because the boric acid in the raw batch chemicals oxides had already released the chemically bound water during the first vitrification evolution to make the cullet used to produce the frit.

The induction heating power to the cylinder and cone bottom induction heating coils was then ramped at 10/4095 increments per minute (about 0.25%/min output) to achieve a nominal temperature increase of 5 to 10°C per minute at the Pt/Rh vessel control thermocouple (T4). A batch bed thermocouple (T1), located along the centerline and 1 inch above the bottom of the CIM vessel, was used to monitor the temperature within the batch bed and eventually provided an indication of the molten glass pool temperature. When the glass pool temperature reached 1380°C, air bubbling through the glass was initiated at 0.75 scfh air flow rate to facilitate mixing. The glass was held at 1400°C or greater for 3 hours. Glass pouring was initiated by applying heat to the CIM drain tube. The melter contents were typically discharged into a water-filled stainless steel pail, yielding glass cullet.

The total time required from beginning melter heating to initiation of glass pouring was typically 6 hours 30 minutes. The CIM cool down was achieved by ramping the induction heating power at about 50/4095 increments per minute down to minimum power, then de-energizing the power supplies. The cooling water flow through the induction heating coils was maintained until the indicated vessel temperature was less than 100°C, at which time the cooling water flow was terminated. The CIM typically cooled to less than 100°C within two hours of initiation of the cooling evolution (completion of glass draining). The typical CIM heating profile to process LaBS Frit X batch chemicals is shown in Figure 2. The CIM temperature and power input data for this run are shown in Table 26 in the Appendix.

Table 4 Initial Batch Quantity and Bed Height within 14-Inch Tall CIM Vessel

Run	Material Added (g)	Initial Batch Bed Height (in)	Material Batched
1	2170	7	Batch Chemicals
2	2193	7.75	Batch Chemicals
3	3264	11.25	Batch Chemicals
4	2000	5	140 mesh Frit
5	2000	5	140 mesh Frit
6	2039	5	140 mesh Frit
7	6020	9.5	Glass Cullet
8	3000	10	Batch Chemicals
9	3100	10	Batch Chemicals
10	2600	8.5	Batch Chemicals
11	2600	8.5	Batch Chemicals
12	3189	10.25	Batch Chemicals
13	3191	10.5	Batch Chemicals
14	3000	8.5	Frit X / HfO_2 / NaCl
15	2981	8	Frit X / HfO_2 / Impurities
16	2833	5.75	Glass Cullet from Run 16

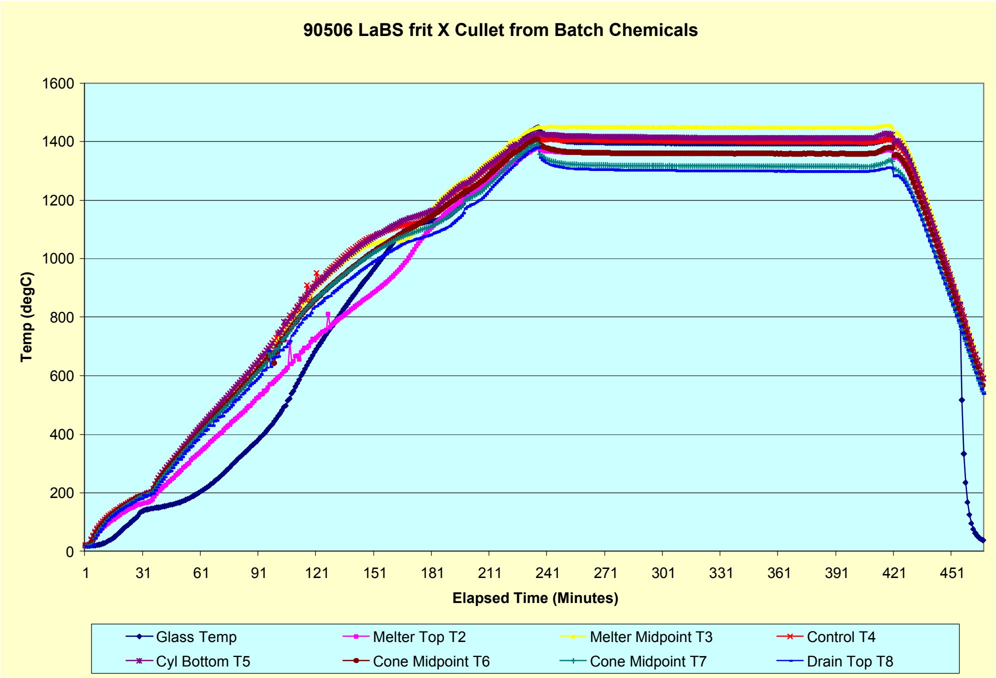


Figure 2 Typical CIM Heating Profile To Process LaBS Frit X Batch Chemical

2.2.3 Melter Process Testing - Frit X with HfO_2 (Molar) Substitution for 9.5 wt% PuO_2

In Runs 4-6, an 1850 gram charge of LaBS Frit X from cullet previously milled to a nominal 140 mesh particle size (<100 microns) was combined with 150 g of HfO_2 powder in a Braun™ mixer to yield LaBS glass where HfO_2 was substituted for 9.5 wt% (molar basis) PuO_2. The nominal 2000 gram charge was added into the CIM at ambient temperature, and the batch bed height was measured to be 5-inches (total height of the melter vessel is 14-inches). The material was subjected to a standard heating schedule for CIM processing of LaBS frit, including 30 minutes initial heating at minimum induction heating power input, followed by a 5 to 10°C per minute temperature increase to 1400°C, and finally 3 hours mixing with an air bubbler while at 1400°C. The vitrified glass product was discharged into a pail of water, allowed to cool, and then dried. Nominally, 2000 g of glass was produced in each run.

2.2.4 Melter Process Testing - Instrumented Canister Pour

Run 7 was performed to vitrify 6 kg of LaBS Frit X cullet for the purpose of pouring into a stainless steel canister and measuring the heat emitted by the canister. A 19.5" by 3" OD canister (1/16" wall thickness) was instrumented with three type-R thermocouples contacting the outer can wall at the 4", 9" and 13" elevations. 6020 g of LaBS Frit X cullet (produced from raw batch chemicals in Runs 4-6, with additional HfO_2 added to represent 9.5 wt% PuO_2 on a molar basis) was charged into the CIM, resulting in a 9.5" bed height (of 14" total in CIM vessel). The cullet was heated to 1400°C in 3 hours 50 minutes and then air bubbling was initiated at 0.75 scfh to homogenize the glass for an additional 2 hours at 1400°C. Induction heating power was then applied to the drain tube induction heater, and glass pouring was established after a short period (less than 1 minute) of initial glass dripping. The pour stream of 17 minutes duration filled the canister with 13.75" of glass (5991.7 g). The peak temperature indicated by the 4" elevation canister thermocouple was 594°C, and the 9" elevation thermocouple peaked at 626°C. The 13" elevation thermocouple peaked at 440°C due to the limited quantity of glass poured only filling the canister to 13.5" elevation. The goal for completely filling a canister is to pour glass to a 17.5” elevation, or 2” from the top of the canister. The can temperatures as the canister cooled were recorded by computer and are shown in Figure 3.

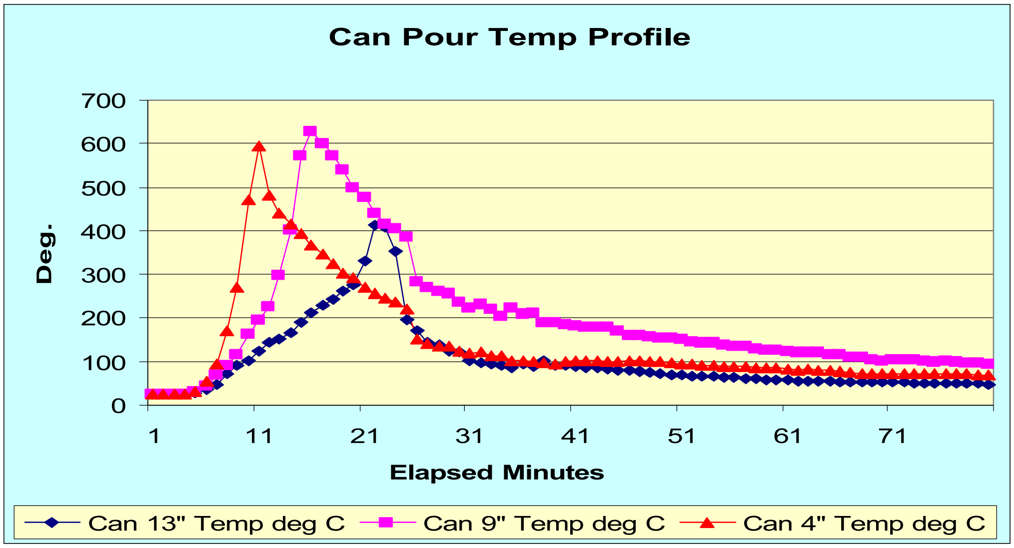


Figure 3 Prototype Canister Heating and Cooling Temperature Profile

2.2.5 Melter Process Testing - Produce Cullet Feed for Offgas Sampling Testing

As with Runs 1-3, Runs 8-13 were performed to produce cullet from LaBS Frit X batch chemicals that was milled to nominally 20 microns particle size frit. The resultant frit was used as feed for offgas impurities testing (Runs 14-16). Nominally 2600 to 3200 g of LaBS Frit X blended/ball milled batch chemical oxides were charged to the empty CIM melter vessel. The yields of these batches are given in Table 5. Again, it should be noted that the use of boric acid as the source of boron for the glass resulted in weight loss during the melting process. (The batch bed heights for the CIM tests are shown in Table 4.) Then, the vessel cylinder and conical bottom induction heaters were energized at an initial power input of 0/4095 (minimum induction power) for 30 minutes to ensure any moisture present within the batch is driven off. After the initial heating at minimum induction heating power input, the vessel and cone bottom induction heating power inputs were set to 350/4095 and power ramping initiated at a rate increase of 10/4095/minute for both zones. The Pt/Rh vessel was heated at a rate of 5 to 10°C per minute to 1380°C. For each run, the glass pool temperature reached the targeted 1380°C temperature at the vessel induction heating power input of 2200/4095 (216 volts, 32 amps, 6.91 kW) and the cone bottom induction heating power input of 2100/4095 (185 volts, 12 amps, 2.22 kW). A Pt/Rh bubbler tube was inserted into the glass pool to a depth of one inch above the bottom of the CIM vessel, and air bubbling was initiated at 0.75 scfh for three hours. Upon initiation of air bubbling, the glass pool temperature very quickly reached isothermal conditions throughout the volume of glass, with the pool thermocouple (T1) indicating 1400°C. The glass pool temperature gradually increased to 1450°C at the constant induction heating power inputs.

At the completion of three hours at 1400°C - 1450°C with air bubbling, the induction heating power to the drain tube was set to 1000/4095 (130 volts, 4 amps, 0.6 kW). Then the drain tube induction heating power was ramped at 50/4095/minute to a target of 1850/4095. Cooling air was applied to the lower drain tube at 50 SCFM to prevent the glass from draining until the upper section of the drain tube was sufficiently heated to assure a clean pouring initiation. When the drain tube induction heating power input reached 1850/4095 (172 volts), the drain cooling air was turned off and glass pouring began quickly thereafter (less than 30 seconds later). The contents of the vessel were poured into stainless steel pails of water to produce cullet. The drain tube was cooled by the application of the drain cooling air to freeze the last of the glass pour to provide a glass plug inside the drain tube for the next CIM run.

At the conclusion of the draining evolution, the drain tube induction heating power was immediately set to OFF. The vessel and cone bottom induction heating power inputs were ramped to 0/4095 at a rate of 50/4095/minute. Once 0/4095 induction heating power input was reached, both power supplies were set to OFF. The cooling water supply to the vessel, cone bottom and drain induction heating coils was maintained until all thermocouples indicated 200°C or less. The bubbler assembly and melt pool thermocouple (T1) were extracted from the vessel during the cooling cycle to prevent either from adhering to the interior vessel wall should they have contacted the vessel wall with glass residue present.

Table 5 LaBS Frit X Cullet Yield From Batch Chemicals

Run #	Batch Chemicals Processed (g)	Cullet Yield (g)	% Yield By Mass
8	3000	2673	89.1
9	3100	2757	88.9
10	2600	2326	89.4
11	2600	2288	88.0
12	3189	2803	87.9
13	3191	2791	87.5

2.2.6 Cullet Milling to Produce Frit

The cullet produced by Runs 8-13 was shipped to Union Process Inc. to be size reduced using an attritor mill. The attritor mill is the preferred technology for mixing and milling for the PDP program. The cullet was divided into batches ranging from 500 to 2000 g for processing in the attritor mill. A model SG-1 attritor mill with tungsten-carbide arms and an alumina bucket liner was used. The grinding media was 3/8” alumina. The majority of the cullet was fed to the mill after screening through an 8 mesh sieve. The mill was run for approximately 6 minutes and then discharged. The resulting product was screened with a 100 mesh sieve, with the +100 material recycled back into the mill for further size reduction. An example of the typical particle size distribution is shown in Table 6.

Table 6 Typical Particle Size Distribution from Attritor Milled LaBS Frit X Cullet

% Less Than Indicated Size	Particle Size (micron)
10	3.454
20	7.508
30	11.82
40	16.78
50	22.63
60	29.60
70	38.32
80	50.51
90	74.16
95	105.9

The powder from the individual attritor mill batches was blended together. Additional data from the individual attritor mill batches can be found in the trip report from Union Process.[7]

2.3 Offgas Sampling System

2.3.1 Offgas Sampling System Fabrication

Runs 14-16 (NaCl, Rocky Flats, Remelt Runs) were conducted to sample the offgas emissions that evolve during the vitrification of LaBS Frit X blended with HfO_2 (as a surrogate for PuO_2) and expected impurities. Modifications were made to the CIM to accommodate an EPA gas sampling train. Offgas sampling was performed using a modification of EPA Source Sampling Method 26.[8] This EPA method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2]. Bromine was not present in these tests. A diagram of the offgas sampling system is shown in Figure 4.

The top of the melter was replaced with a 3/8” thick quartz plate with a 1” offgas vent hole and two smaller penetrations to accommodate the glass melt thermocouple and the bubbler (see Figure 5). A 1” thick sheet of M-board insulation was placed on top of the quartz plate. A quartz cylinder was placed into the hole in M-board and quartz plate so that the offgases leaving the melter would not contact the M-board insulation. The offgases were collected by a Pyrex™ glass sampling funnel that was positioned above the melter vent penetration, and the balance of the glasswork and impinger vessels were positioned in close proximity to the melter by the addition of a new support platform (see Figure 6).

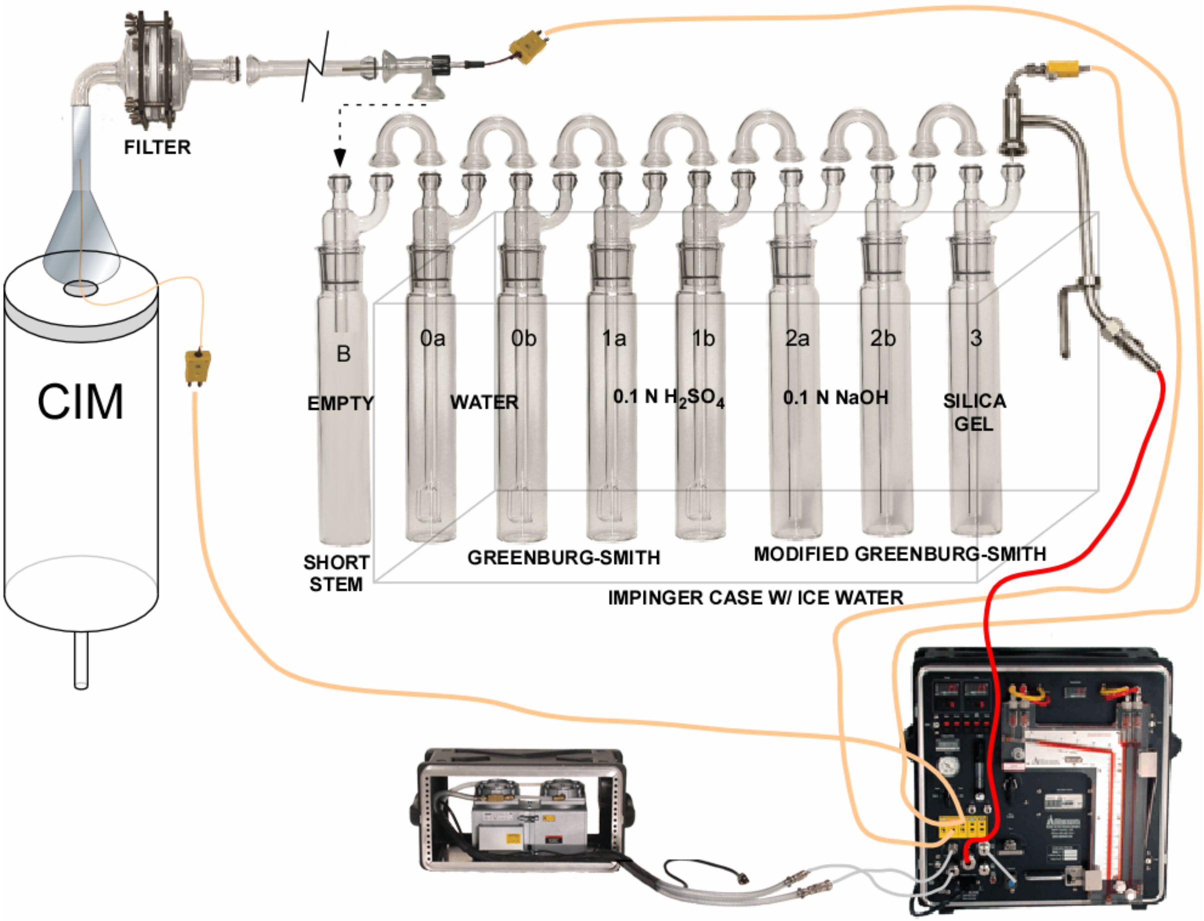


Figure 4 Modified Method 26 Sampling Train

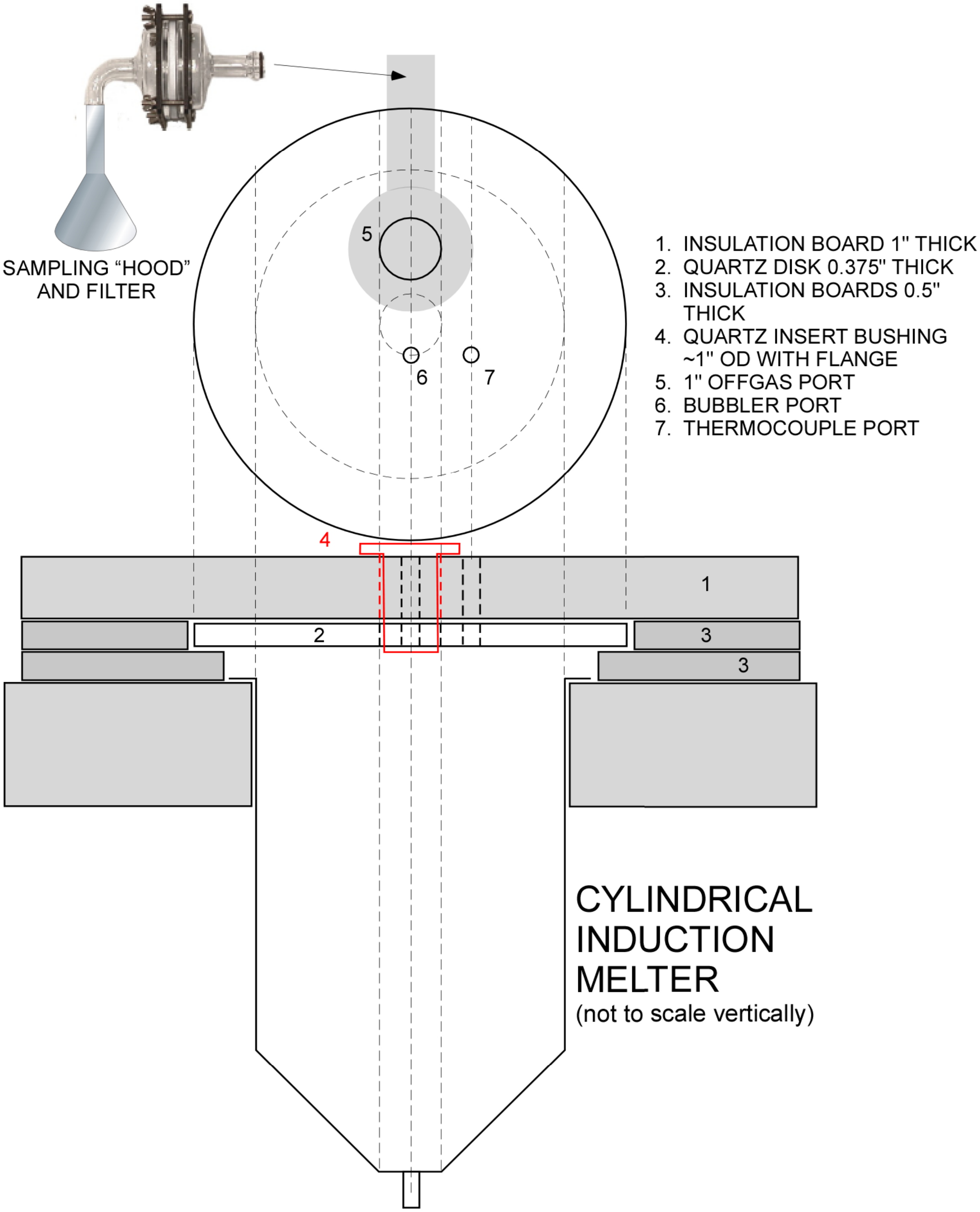


Figure 5 CIM Top Head Offgas Sampling Configuration

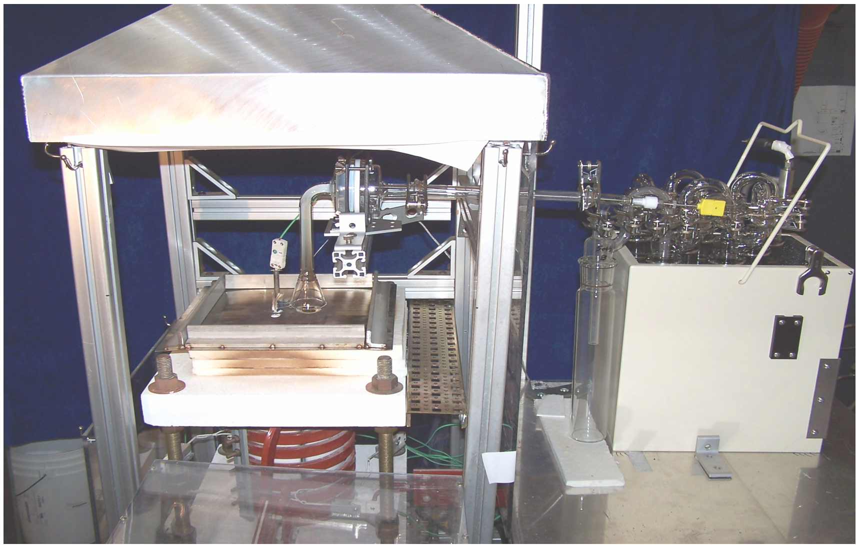


Figure 6 Offgas Sample Collection Equipment

A 3" diameter quartz fiber on Teflon™ mesh filter was used to collect particulate. The filter papers have 99.95% efficiency for dioctyl phthalate (DOP) particles at 0.3 μm. The offgas was then passed through an empty impinger, two water impingers, two 0.1N (0.05M) sulfuric acid (H_2SO_4) impingers, two 0.1N sodium hydroxide (NaOH) impingers, and then a silica gel impinger to remove any water vapor remaining in the gas. All except the empty impinger were kept at near 0 °C in an ice bath. The gas flowrate varied from around 0.15 to 0.6 ft^3/min (cfm). The flowrate was measured with an orifice meter and a dry gas meter.

2.3.2 Offgas Sampling System Operation

Because the stack sampling system collected the entire offgas from the melter, isokinetic sampling was not required, so control of the sampling rate was not critical so long as all of the offgas was collected. During filter and impinger changes, there were short (<5 minutes) periods where the offgas was not collected.

The particulate matter recovered from the filter and filter inlet were analyzed for halides, other anions, metals, and by SEM/EDS. This analysis is not part of EPA Method 26; these methods quantify only the hydrogen halides and halogens. There is no EPA method for halide salts. The total particulate mass was also measured approximately by weighing filter assembly before and after sampling.

The first empty impinger was used to protect the melter from accidental flow reversal in the sample system that could have resulted in water being sprayed onto the top of the melter. The empty impinger and the outlet of the filter were rinsed with water and analyzed with the water impinger contents.

The water impingers were added to the EPA method to help distinguish between chloride from HCl vapor and from NaCl, KCl, or other chloride salt; the EPA method is not designed to look for salts. Increases in the acidity of the water is directly indicative of the amount of HCl and HF in the offgas.

The halides were quantified by Ion Chromatography (IC); nitrate, sulfate, and phosphate were also measured by IC. Metals were quantified by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Samples containing solids were analyzed for total species by dissolving the solids with a few drops of HNO_3 and also for soluble species by first filtering out the solids.

The acid impingers are designed to remove the hydrogen halide vapors, while the basic impingers remove the halogens (Cl_2). Chlorine has a very low solubility in the acidic solutions and should pass through to the alkaline solution where it is hydrolyzed to form a proton (H^+), the chloride ion, and hypochlorous acid (HClO):

$$Cl_2 + H_2O \qquad H^+ + Cl^- + HClO$$

Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypochlorous acid to form a second halide ion such that two chloride ions are formed for each molecule of chlorine gas. Table 7 summarizes the sample and analyses performed. All chemical analyses except total acid were performed by the Process Science Analytical Laboratory; the total acid analyses, X-Ray Diffraction (XRD), and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS) were performed by SRNL- Analytical Development (AD).

Table 7 Sample Preparation and Analyses

Sample	Preparation	Analyses
Filter – Particulate	none	total mass XRD SEM/EDS
Filter – Particulate	dilution & dissolution (acidification)	IC (except nitrate) ICP-AES
Filter – Particulate	dilution & filtration	IC ICP-AES
Water Impingers (+ empty impinger)	dilution	Total Acid IC ICP-AES
Acid Impingers	dilution	Total Acid IC (except sulfate) ICP-AES (except sulfur)
Basic Impingers	dilution	IC
Basic Impingers	reaction with sodium thiosulfate	IC (except sulfate)

Based on results from monitoring by SRNL Industrial Hygiene, an offgas collection hood was fabricated and installed above the existing CIM Lexan™ shielding barriers to ensure that emissions are captured during the periods when the offgas sampling filters are being replaced (See Figure 7). A Job Hazards Analysis,[9] Environmental Evaluation Checklist,[10] and Safety Inspection were completed and approved by management prior to the initial offgas sampling run.

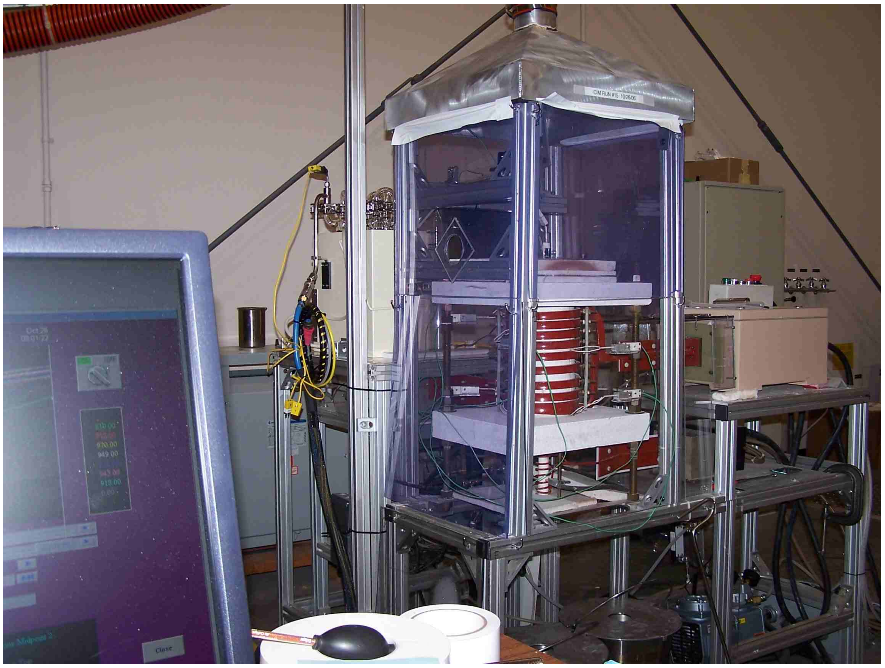


Figure 7 CIM Lexan™ Shield Barriers and Fume Hood

Three offgas sampling test runs were conducted with the CIM in this initial phase of work. In each run, LaBS Frit X was blended with impurities additions for the purpose of sampling the particulate and vapors emitted from the melt (see Figure 8). Information obtained from these tests will support the design of the offgas handling system required for the PDP. Information obtained in this phase will also guide follow-on experimental work.

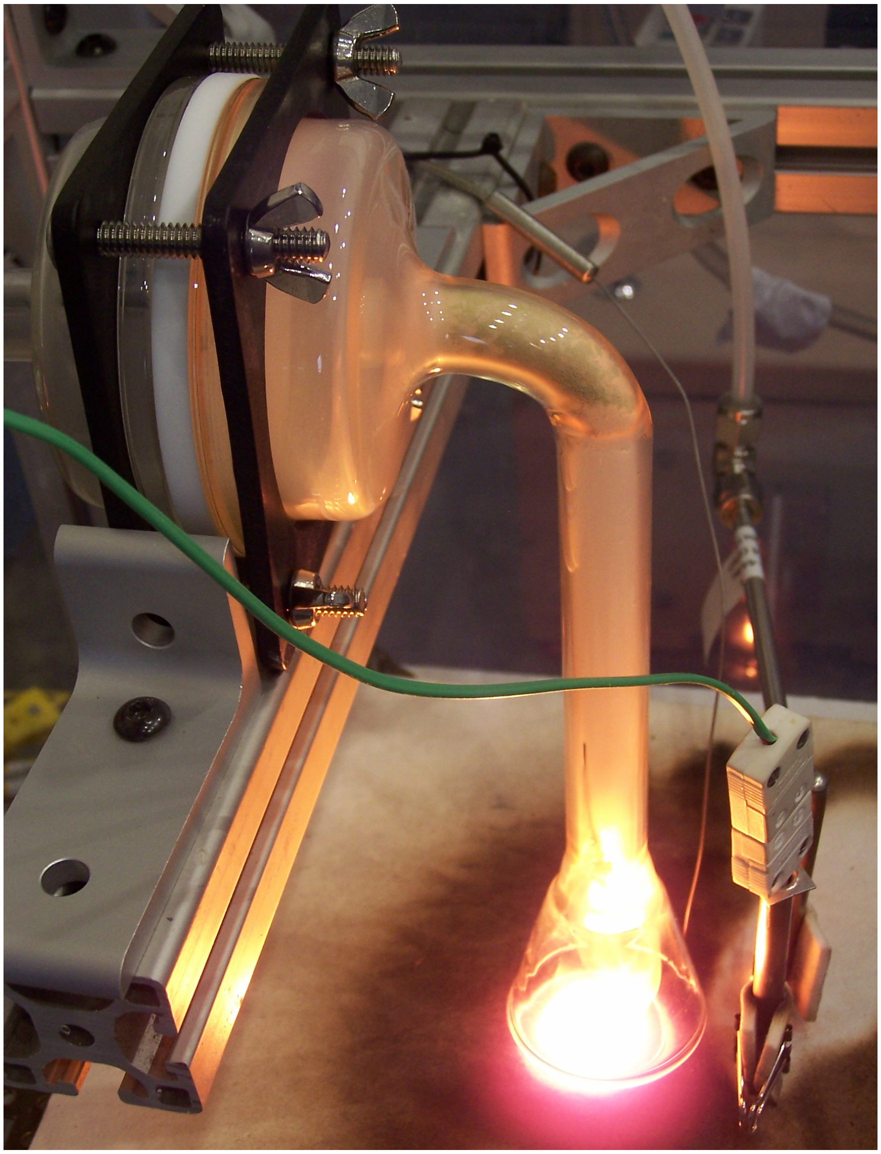


Figure 8 Offgas Emissions Quartz Collection Funnel and Filter

2.4 Batching of Frit X, Hafnium Oxide, and Impurities

Three runs (Runs 14-16) of the CIM were performed with Frit X, HfO_2, and impurities. The first impurity run (NaCl Run) included only NaCl as an impurity, while the second run (Rocky Flats Run) included impurities to approximate the composition of Rocky Flats can B5495.[11] The third run (Remelt Run) re-melted the glass product from the Rocky Flats Run.

The mass of each feed species for the NaCl and Rocky Flats Runs are shown in Table 8. The total amounts of feed and the final glass mass are also given. The nominal target and measured composition of the Frit X used is shown in Table 9.

Table 8 Feed Compositions for NaCl and Rocky Flats Runs

Component	NaCl Run		Rocky Flats Run		Remelt Run
	Mass (g)	Wt% in Feed	Mass (g)	Wt% in Feed	Mass (g)
Total Final Glass (measured)	**2927.8**	**NA**	**2924.9**	**NA**	**2830.4**
Total Initial Feed	**3000 (2981)**[†]	**NA**	**2981**	**NA**	**2833**
Frit X	2700	90.0	2733.3	91.7	NA
HfO_2 *	225	7.5	153.4	5.14	
Σ Impurities	75.0	2.5	94.28	3.16	
$CaCl_2 \cdot 2H_2O$	0	0	4.76	0.16	NA
CaF_2	0	0	6.56	0.22	
Cr_2O_3	0	0	5.46	0.18	
CuO	0	0	0.304	0.01	
Fe_2O_3	0	0	2.98	0.10	
KCl	0	0	26.93	0.90	
MgOHCl	0	0	13.68	0.46	
MoO_3	0	0	0.609	0.02	
NaCl	75.0	2.5	26.33	0.88	
NiO	0	0	4.47	0.15	
Na_3PO_4	0	0	0.703	0.024	
WO_3	0	0	1.49	0.05	

* HfO_2 is present in the frit and is also used as the surrogate for PuO_2.

[†] Initial mass target was 3000 g; initial mass actually added to melter not measured; assumed to be similar to the Rocky Flats Run

Table 9 Target and Measured Composition of Frit X

Element	**Target (wt%)**	**Measured 1 (wt%)**	**Measured 2 (wt%)**	**Mean (wt%)**
Al	5.29	6.08	6.27	6.18
B	4.04	3.89	3.93	3.91
Gd	11.71	11.60	11.60	11.60
Hf	5.94	5.41	5.66	5.54
La	16.20	16.10	16.10	16.10
Nd	12.86	12.30	12.20	12.25
Si	9.35	9.66	9.81	9.74
Sr	2.11	2.08	2.06	2.07
Cu	0	0.04	NA	0.04

Oxide	**Target (wt%)**	**Mean (wt%)**
Al_2O_3	10.00	11.67
B_2O_3	13.00	12.59
Gd_2O_3	13.50	13.37
HfO_2	7.00	6.53
La_2O_3	19.00	18.88
Nd_2O_3	15.00	14.29
SiO_2	20.00	20.83
SrO	2.50	2.45
CuO	NA	0.05
TOTAL	100.0	100.6

(Cr, Fe, Ni, Ca, K, Mg, Mn, Mo, P, Pb, S, Ti, Zn, Zr all below detection limits)

The documented composition of the Rocky Flats B5495 is compared to the actual composition of the feed used for the Rocky Flats Run (excluding the Frit X) in Table 10. Some approximations to the actual composition had to be made. The Pu content is a combination of PuO_2 and PuF_4; HfO_2 is used as a surrogate for PuO_2 in the simulant tests, but HfF_4 was not available. To add more fluorine (F), CaF_2 was added, which resulted in the Ca content of the simulant being about 3.6 times higher than the target. The actual frit content of the total feed was 91.7 wt% versus the target 90.0 wt%. This difference was due to unintentionally leaving out the Pu from PuF_4 and not adding an equivalent amount of Hf for the Pu. The amount of HfO_2 added was equivalent to the amount of PuO_2 present on a molar basis.

Magnesium chloride $MgCl_2$ cannot be added in the anhydrous form due to its hygroscopic nature; only the hexahydrate can be used in non-inerted atmospheres. Because this impure Pu stream has been fired at high temperature, it was deemed likely that the MgO and $MgCl_2$ could have formed the hydroxychloride MgOHCl, so MgOHCl was used in place of the MgO and $MgCl_2$. MgOHCl is also much easier to handle as it is a refractory non-hygroscopic solid. Use of MgOHCl resulted in the chloride content of the simulant being about 20% higher than the target.

Anhydrous sodium phosphate Na_3PO_4 was substituted for phosphorus pentoxide P_2O_5, again due to the hygroscopic nature of P_2O_5. This substitution resulted in 3% more Na than the target. Calcium chloride dihydrate $CaCl_2 \cdot 2H_2O$ was used rather than the anhydrous form because the anhydrous material was not available.

Overall, the impurities accounted for about 38 wt% of the simulated Pu feed compared to the target value of about 29.4 wt%. The difference is due to the substitutions described above. The Pu stream is assumed to be completely dry, but the actual amount of water associated with it is not known. No additional water was added to the simulant other than any water that was associated with the reagents and any water that may have been adsorbed during handling in the laboratory.

Table 10 Comparison of Rocky Flats Run Feed Composition (Actual) and Documented Rocky Flats B5495 Composition (Target)

Feed Component	Target Wt% of Feed	Actual Wt% of Feed	Target Wt% of Feed + Frit	Actual Wt% of Feed + Frit
Al_2O_3	0.98	NA	0.0982	NA
$CaCl_2$	1.18	NA	0.118	NA
$CaCl_2 \cdot 2H_2O$	(1.57)[a]	1.92	NA	0.160
CaF_2		2.65	0	0.220
CrO_3	2.36	NA	0.236	NA
Cr_2O_3		2.20	0	0.183
CuO	0.100	0.123	0.010	0.010
Fe_2O_3	0.98	1.20	0.098	0.100
KCl	8.87	10.9	0.887	0.904
MgO	2.36	NA	0.236	NA
MgOHCl	NA	5.52	0	0.459
MoO_3	0.20	0.246	0.020	0.020
NaCl	8.67	10.6	0.867	0.883
NiO	1.47	1.81	0.147	0.150
P_2O_5	0.100	NA	0.010	NA
Na_3PO_4	(0.231)[b]	0.284	NA	0.024
SiO_2	1.57	NA	0.157	NA
WO_3	0.49	0.602	0.049	0.050
PuF_4	4.43	NA	0.443	NA
PuO_2	66.2	NA	6.62	NA
HfO_2	NA	61.9	NA	5.14
Frit X	NA	NA	90.0	91.7
Total Impurities	**29.4**	**38.1**	**2.94**	**3.16**
Impurities + HfO_2	**100**	**100**	**10.0**	**8.31**
TOTAL	**100**	**100**	**100**	**100**

[a] $CaCl_2 \cdot 2H_2O$ that would correspond to the $CaCl_2$

[b] Na_3PO_4 that would correspond to the P_2O_5

2.4.1 Chronology of NaCl Run

The NaCl Run processed approximately 3000 g of feed which was charged into the CIM, resulting in a 8.5" bed height (of 14" total in the CIM vessel). The batch was heated to about 1400°C (following the standard heating rate cycle employed when producing LaBS cullet from batch chemicals). Air bubbling was then initiated at 0.75 scfh to homogenize the glass for an additional 3 hours at 1450ºC (per T1). During glass pouring, glass samples were collected at the initiation of pouring, mid-way into the pour, and as the final glass drips were deposited. The offgas was sampled throughout the entire vitrification run. A detailed account of the offgas sampling results is presented in Section 3.1, and events and observations are listed in Table 11.

Table 11 NaCl Run Events/Observations

Elapsed Run Time (min)	Vessel Temp (T4) (ºC)	Bed Temp (T1) (ºC)	Run Feature / Observation
0	18	18	~3000g batch – begin heating at 0/4095
30	248	57	Set induction heating power to 350/4095
31	264	60	Initiate temp ramping at 5-10°C/min.
164	1129	975	OG emissions visible - captured
194	1271	1216	Visible salt deposits in OG collection
226	1399	1389	Initiate air bubbler at 0.75 scfh
232	1404	1445	1st OG filter change out
294	1407	1458	Impinger set / 2nd OG filter change out
398	1405	1457	2nd Impinger set / 3rd OG filter change
413	1404	1457	Initiate drain tube heating
421	1404	1461	Glass pouring began – pour sample #1
425	1407	1463	Pour sample #2 collected
426	1409	1463	Pour concluded – pour sample #3
427	1412	1463	OG sampling concluded

2.4.2 Chronology of Rocky Flats Run

The Rocky Flats Run (Run 15) processed a 2981 g batch consisting of LaBS Frit X with chemical additions representative of a Rocky Flats Can B5495 composition. The same heating and sampling schedule was followed as was employed with the previous NaCl addition test. The offgas was sampled throughout the entire vitrification run. Particulate and vapors were still evident by visual observation at the completion of three hours air bubbling at 1450ºC. Part way through the run, the bubbler air flow was reduced to about 0.35 scfh to see if the lower flowrate would visibly change the appearance of the offgas particulate emissions. No noticeable change occurred. During glass pouring, glass samples were collected at the initiation of pouring, mid-way into the pour, and as the final glass drips were deposited. A detailed account of the offgas sampling is presented in Section 3.1, and events and observations are listed in Table 12.

Table 12 Rocky Flats Run Events/Observations

Elapsed Run Time (min)	Vessel Temp (T4) (ºC)	Bed Temp (T1) (ºC)	Run Feature / Observation
0	19	65	2981g batch – begin heating at 0/4095
30	251	97	Set induction heating power to 350/4095
31	267	101	Initiate temp ramping at 5-10°C/min.
126	899	680	Deposits on OG filter and glass funnel
179	1179	1125	Visible dense vapor emission from melter
198	1287	1231	1st OG filter change out
219	1382	1366	Initiate air bubbler at 0.75 scfh
227	1390	1435	Reduced bubbler flow to 0.35 scfh
230	1390	1441	2nd OG filter change out
283	1373	1434	Change out impinger set
345	1371	1432	3rd OG filter change out
380	1371	1433	4th OG filter change out
396	1371	1432	Initiate drain tube heating
413	1372	1434	Glass pouring began – pour sample #1
416	1375	1435	Pour sample #2 collected
419	1376	1436	Pour concluded – pour sample #3
420	1376	1436	OG sampling concluded

2.4.3 Chronology Remelt Run

The Remelt Run (Run 16) processed the glass produced as the product from the Rocky Flats Run. At the completion of three hours of air bubbling in the glass pool at 1450ºC in the Rocky Flats Run, particulate and vapors were still being emitted by the melt. Therefore, for the Remelt Run, the glass from the Rocky Flats Run was reheated in the CIM to 1450ºC, mixed by air bubbling at 0.75 scfh for three hours, and offgas emissions sampled throughout the run. During glass pouring, glass samples were collected as with prior offgas sampling test runs. A detailed account of the offgas sampling is presented in Section 3.1, and events and observations are listed in Table 13.

Table 13 Remelt Run Events/Observations

Elapsed Run Time (min)	Vessel Temp (T4) (ºC)	Bed Temp (T1) (ºC)	Run Feature / Observation
0	38	17	2833g glass – begin heating at 0/4095
30	249	102	Set induction heating power to 350/4095
31	266	105	Initiate temp ramping at 5-10°C/min.
165	1123	1058	Yellow/brown deposits on OG filter
175	1177	1121	Visible deposits on OG glass funnel
220	1375	1386	Initiate air bubbler at 0.75 scfh
248	1390	1455	1st OG filter change out
350	1379	1447	2nd OG filter change out
400	1378	1448	Initiate drain tube heating
400	1378	1448	OG emissions greatly reduced
420	1378	1450	Glass pouring began – pour sample #1
423	1381	1451	Pour sample #2 collected
425	1382	1450	Pour concluded – pour sample #3
426	1382	1450	OG sampling concluded

3.0 RESULTS

3.1 Offgas Sampling Results

The offgas samples were collected and analyzed as described in Section 2.3.2. The results are documented in laboratory notebook WSRC-NB-2006-00030[12]. For each run, several particulate samples were taken for each of one or two sets of impingers, as summarized in Table 14.

Table 14 Summary of Sampling Sets

Run	Impinger Sets	Particulate Filters
NaCl Run	2	4
Rocky Flats Run	2	6
Remelt Run	1	3

The amounts of each offgas species (element) collected per kg of glass produced in the Rocky Flats Run are shown in Table 15. The fraction as wt% of each species present in the feed that was evolved to the offgas is also given. Based on the chemical analyses, about 1.72 wt% of the feed was volatilized to the offgas system; based on the mass loss from the feed to glass (feed mass minus glass mass), the amount volatilized is estimated to be 1.92 wt%. Of the total impurity addition of 3.16 wt%, the offgas species constitute 54-61% of the impurities. The major constituents in the offgas particulate were Cl, K, and Na, while Cl and F predominated in the offgas scrub solutions. All of the frit components were found in very low concentrations in the offgas. Except for Hf and boron (B), all were less than 0.03 wt% in the offgas. Hf is likely to be higher due to physical entrainment of HfO_2 particles while boron is higher due to the known volatility of boron at the melter temperatures. To check whether physical entrainment of HfO_2 is likely, particle size analysis of the HfO_2 will be performed and documented in a future report. The decontamination factors (DF) for the melter to offgas are also given. The sum of the elements for the particulate (6541 mg/kg) was very close to the particulate mass measured (6051 mg/kg).

Table 15 Offgas Species Collected from the Rocky Flats Run

Shaded components are Frit X species

	Offgas Particulate (mg/kg glass)	Offgas Scrubbers Total (mg/kg glass)	Offgas Total (mg/kg glass)	Offgas / Feed (wt%)	Decontamination Factor
Mass Loss (Feed - Glass)	NA	NA	19146	**1.92**	NA
Mass Measured	6051	NA	NA	NA	NA
Σ Elements	6541	5565	12107	**1.72**	58.0
Cl + F	3098	5510	8608	62.0	1.61
K + Na	2830	29.7	2860	34.2	2.93
Cl	3086	5337	8422	65.9	1.52
Cu	47.8	0.50	48.3	58.2	1.72
K	2101	17.8	2118	43.9	2.28
Mo	32.0	1.60	33.6	24.3	4.12
Na	730	11.9	742	20.9	4.77
Ni	241	2.71	243	20.2	4.94
F	12.2	173	185	17.0	5.89
Fe	24.4	0.45	24.8	3.48	28.7
Cr	37.9	6.09	43.9	3.44	29.1
W	5.50	0.19	5.69	1.41	71.1
Ca	2.10	0.20	2.30	0.52	192
P	0.09	0	0.09	0.20	510
B †	52.1	7.38	59.5	0.16	614
Hf	156	0.03	156	0.16	615
Mg	0.64	0	0.64	0.043	2316
Sr	5.73	0.11	5.85	0.030	3309
Si †	0.26	4.76	5.03	0.0055	1.81E+04
Al	1.33	0.24	1.57	0.0027	3.66E+04
La	0.59	0	0.59	0.00039	2.56E+05
Gd	0.31	0	0.31	0.00029	3.46E+05
Nd	0.31	0	0.31	0.00027	3.69E+05
Pb*	0.54	0	0.54	NA	NA
S*	1.11	1.78	2.89	NA	NA
Zn*	3.54	0	3.54	NA	NA

* not added to feed † B & Si in scrubbers possibly from glassware

Table 16 shows the offgas species collected in the NaCl Run. Based on the chemical analyses, about 1.79 wt% of the feed was volatilized to the offgas system, while the amount volatilized based on the feed and glass masses was 1.82 wt%. These amounts correspond to an impurity loss of ~72% of the added 2.5 wt%. The losses of Na and Cl were similar to the values found for the Rocky Flats Run. The DFs for boron and Sr were again the highest for the frit components. The species with NA for the decontamination factor were not intentionally added to the feed, but some were present nonetheless. The elements K, Fe, and Cu were present at higher than expected amounts. The K may have been an impurity in the NaCl used. The source of Fe may be from blending of the frit and HfO_2 in ferrous metal equipment or from the HfO_2 used (99% pure). Frit analysis (prior to blending) showed no detectable Fe. The HfO_2 has not been analyzed for impurities. The Cu could have come from frit screening on brass sieves. Brass contains both Cu and Zn, and Zn was found in the offgas particulate even though it was not added; the ratio of Zn:Cu was 0.25 which is in the range of a typical brass.

Table 16 Offgas Species Collected from the NaCl Run

Shaded components are Frit X species

	Offgas Particulate (mg/kg glass)	Offgas Scrubbers Total (mg/kg glass)	Offgas Total (mg/kg glass)	Offgas / Feed (wt%)	Decontamination Factor
Mass Loss (Feed – Glass)	NA	NA	18171	**1.82**	NA
Mass Measured	3354	NA	NA	NA	NA
Σ Elements	6725	6041	12767	**1.79**	55.8
Cl	3973	6028	10001	64.4	1.55
Na	2632	0	2632	26.1	3.83
B †	42.1	5.65	47.7	0.13	756
Sr	18.1	0.085	18.1	0.095	1052
Al	1.00	0.100	1.10	0.0019	5.16E+04
La	1.59	0	1.59	0.0011	9.31E+04
Nd	1.07	0	1.07	0.00095	1.06E+05
Hf	1.08	0.006	1.09	0.00093	1.07E+05
Gd	0.826	0	0.826	0.00077	1.30E+05
Si †	0.234	0.128	0.363	0.00040	2.48E+05
K	24.7	0.178	24.8	NA	NA
Fe	12.3	0.029	12.3	NA	NA
Cu	8.85	0.041	8.89	NA	NA
Zn	2.30	0	2.30	NA	NA
Ca	1.70	0.180	1.88	NA	NA
Ni	1.08	0	1.08	NA	NA
S	0.905	4.31	5.21	NA	NA
W	0.725	0.044	0.769	NA	NA
Pb	0.668	0	0.668	NA	NA
Cr	0.331	0.013	0.345	NA	NA
Mo	0.266	0.027	0.293	NA	NA
Mg	0.245	0	0.245	NA	NA
P	0	0	0	NA	NA
F	0	2.77	2.77	NA	NA

Elements below K in table not added to feed. † B & Si in scrubbers possibly from glassware

In Table 17, the total and soluble particulate from the filter samples for the Rocky Flats Run are shown. The species that were mostly insoluble were Al, Fe, Mo, W and phosphate. The elements F, Cr, and K were partially soluble, while Cl, B, Cu, Ni, Na, and Sr were completely soluble.

The offgas scrub solutions contained primarily HCl and HF, with a small amount of alkali. Overall, the amount of alkali and other metals found in the scrubbers was very small, indicating that the particulate filter efficiency was high. Subtracting the Cl and F from the offgas scrubber total and adding back Cl equivalent to the Na and K present (balance Na^+ & K^+ with Cl^-) gives about 90 mg "non HCl or HF"/kg glass in the scrub solutions. This means that other than HCl and HF, only about 0.8% (90/11582) of the species volatilized were collected in the scrub solutions while 99.2% were collected on the filter.

Table 17 Total and Soluble Particulate from the Rocky Flats Run

Species	Total Particulate (g)	Soluble Particulate (g)	Filtrate / Total (wt%)	Solubility in Water
Cl	9.02	8.67	96.0	completely
F	0.0358	0.0225	62.9	partially
PO_4^{-3}	1.43	0.0805	5.6	insoluble
Al	0.0039	0.0010	25.6	mostly insoluble
B	0.152	0.150	98.6	completely
Ca	0.0036	0.0061	171	completely *
Cr	0.111	0.0745	67.3	partially
Cu	0.139	0.140	101	completely
Fe	0.0713	0.0123	17.2	mostly insoluble
K	6.14	3.71	60.4	partially
Mo	0.0937	0.0122	13.0	mostly insoluble
Na	2.13	2.09	97.7	completely
Ni	0.529	0.704	133	completely *
Sr	0.0139	0.0168	121	completely *
W	0.0161	0.0007	4.1	insoluble

* maximum is 100%; values exceed 100% due to analytical uncertainty

The total offgas particulate and the approximate emission rate for all three runs are shown in Figure 9. The amount of particulate collected at any particular time is very similar for the NaCl and Rocky Flats Runs even though the composition of the impurities was different. The particulate evolution rate for the Remelt Run, which used the glass product from the Rocky Flats Run, was very close to the ending rate in the Rocky Flats Run (~0.8 g/kg glass/h). The maximum particulate rate was about 2.6 g/kg glass/h.

The starting temperatures for the first evidence of particulate emission in each run are interesting. The Rocky Flats Run with the variety of impurities began emitting visible particulate at about 680°C, while the NaCl Run with only NaCl began at 980°C, suggesting that some of the impurities in the Rocky Flats Run may be more volatile than NaCl. The Remelt Run had a longer delay until particulate evolution began at 1170°C. A higher temperature may have been required to release salts embedded in the glass matrix versus the previous runs where the salts were mixed with the glass frit. Figure 10 and Figure 11 show the emission rates for specific elements and also for the fluoride and chloride vapor (HF, HCl).

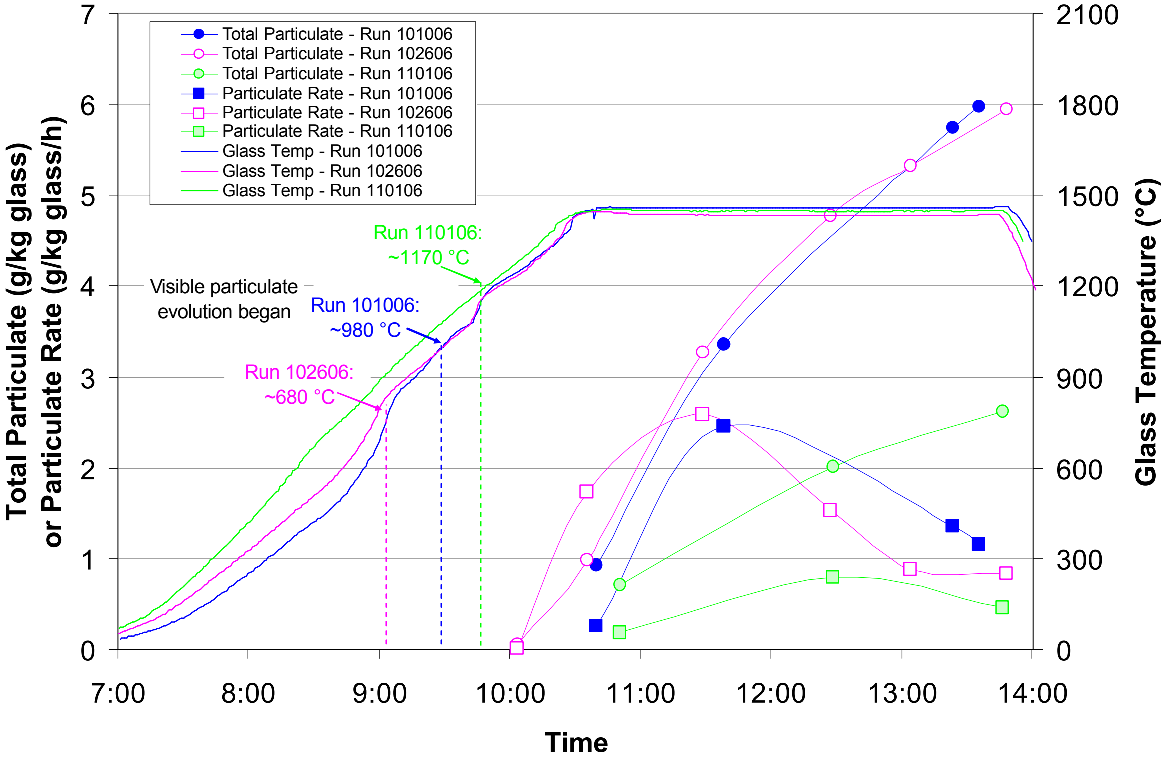


Figure 9 Offgas Particulate Evolution

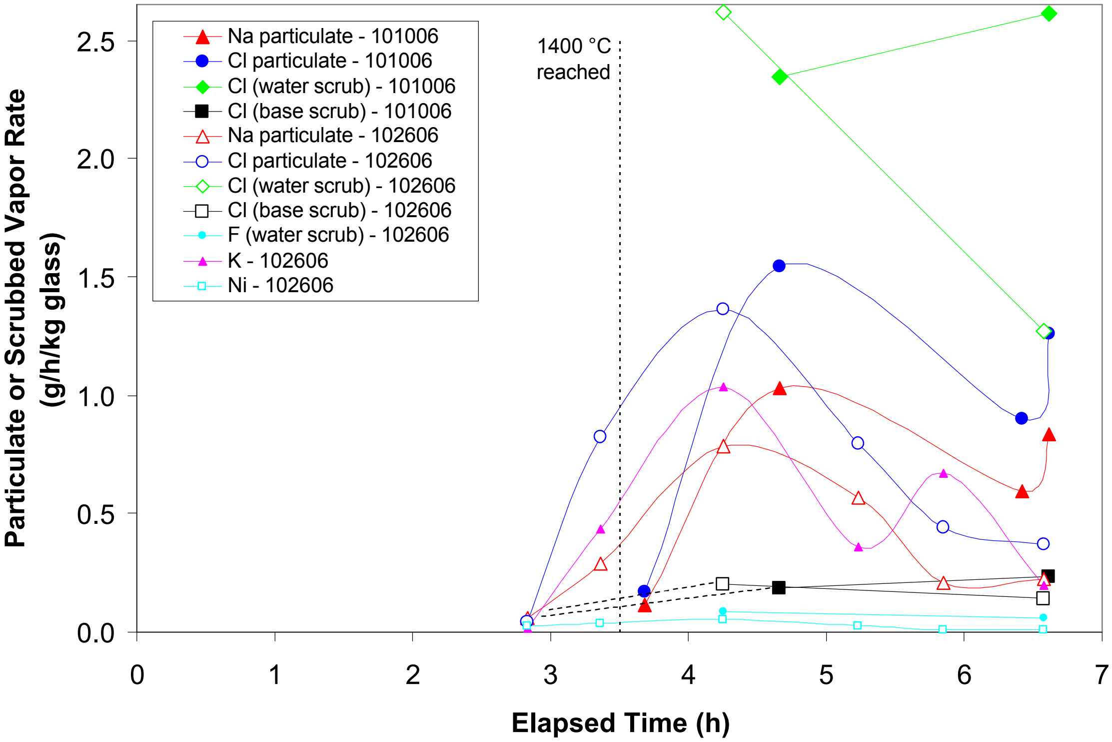


Figure 10 Particulate K, Na, Ni, Cl and Cl, F Vapor Emission Rates for the NaCl and Rocky Flats Runs

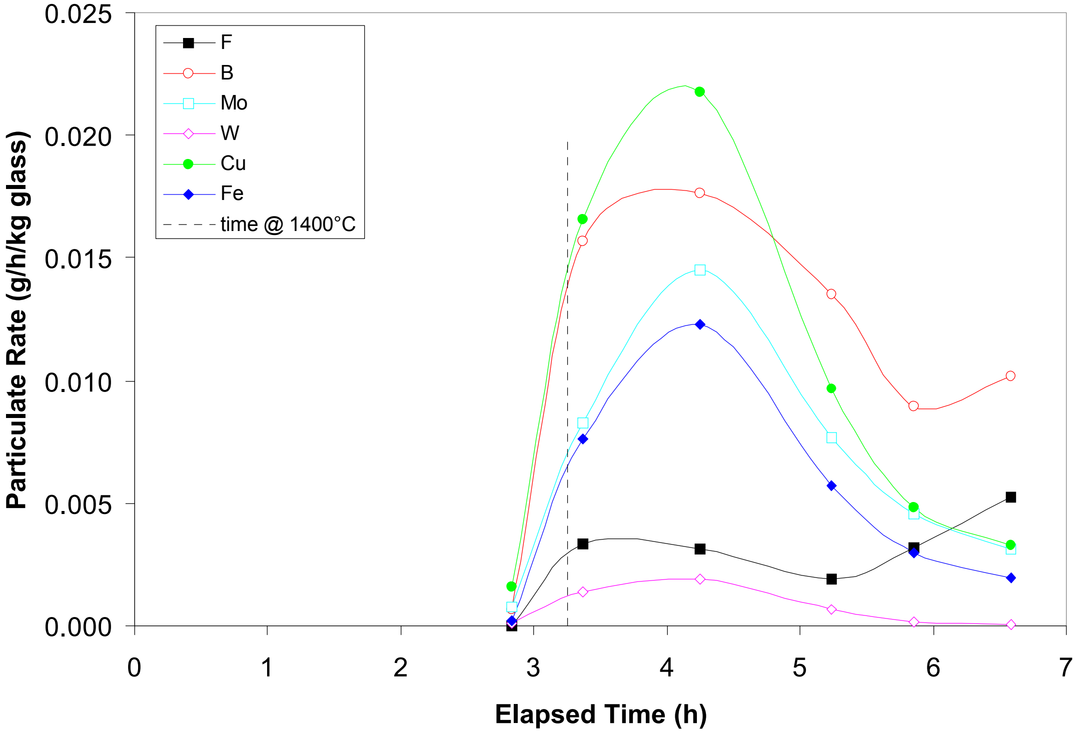


Figure 11 Particulate F, B, Mo, W, Cu and Fe Emission Rates for the Rocky Flats Run

The data in Table 18 show that the total number of moles of alkali (Na, K) collected on the filter papers for the Rocky Flats Run is equal to the moles of halides (Cl, F) collected to within 2.4%. This result indicates that there was very little acid (HCl or HF) on the filter papers. The pH of the filter paper solutions (3.4-5.3) indicates that the maximum acid concentration was about 2.5 x 10^{-4} M. Both the pH data and the halide concentrations in the water impingers show that HCl and HF were produced in the melter. The very low alkali concentrations for the water impingers show that little salt passed through the filter papers into the water impingers. The data in Table 20 show that the chloride collected from the offgas was approximately the same for both runs. The sampling duration for the second impinger sets was about half the first set, but the chloride collected was greater. The rate during the second impinger sets was 2.4 to 3.5 times higher than during the first impinger sets.

The same results for alkali are shown for the NaCl run in Table 19. Again the moles of Na and Cl are essentially the same for the particulate. The amounts of Cl and the pH of the impingers are also similar to the Rocky Flats Run results.

Some salts were observed to pass through an apparent hole in filter #5, and the amount of Na in impinger set #2 (corresponding to filters #4-6) was about 45 mg/L versus ~1 mg/L for set #1. The presence of HCl and HF in the offgas indicates that the NaCl, KCl, and CaF_2 decompose such that some amount the cation Na, K or Ca is retained in the glass, resulting in the Cl and F being evolved as HCl, Cl_2, or HF.

Table 18 Alkali and Halides Collected in the Rocky Flats Run

Sample	Species (mmol)						
	Cl	**F**	**Cl + F**	**K**	**Na**	**K + Na**	**pH[a]**
Filter # 1	9.78	0	9.78	3.12	2.63	5.75	4.5
Filter # 2	36.2	0.274	36.5	17.3	12.5	29.8	3.6
Filter # 3	99.3	0.427	99.7	68.3	34.1	102	3.4
Filter # 4	64.5	0.289	64.8	26.7	24.7	51.4	3.8
Filter # 5	22.3	0.303	22.7	31.0	9.09	40.1	4.5
Filter # 6	22.4	0.591	23.0	10.7	9.77	20.5	5.3
Total Filters	254	1.88	**256**	157	92.8	**250**	NA
Water Impingers	397	26.6	424	0.823	0.908	1.73	0.2, 0.7
Acid Impingers	6.20	0	6.20	0.510	0.606	1.12	1.7, 1.5
Base Impingers[b] – Cl^-, F^-	33.4	0	33.4	NA	NA	NA	4.8, 12.0
Base Impingers[c] – $Cl^- = 2 \times Cl_2$	36.7	NA	36.7	NA	NA	NA	NA
TOTAL	695	28.5	723	158	94.4	253	NA

[a] pH of filtered solids in ~400 mL water; or of impinger liquid before dilution (sets 1 & 2)
[b] Cl^- primarily from Cl_2 by Eq. 1
[c] measured Cl^- after reduction by thiosulfate

Table 19 Alkali and Halides Collected in the NaCl Run

Sample	Species (mmol)		
	Cl	**Na**	**pH[a]**
Filter # 1	52.1	52.5	4.4
Filter # 2	125	129	6.2
Filter # 3	130	132	8.2
Filter # 4	20.8	21.3	8.5
Total Filters	**328**	**335**	NA
Water Impingers	452	0	0.2, 0.9
Acid Impingers	2.6	0	1.8, 1.4
Base Impingers[b] – Cl^-, F^-	36.9	NA	4.6, 10.5
Base Impingers[c] – $Cl^- = 2 \times Cl_2$	43.2	NA	NA
TOTAL	826	335	NA

[a] pH of filtered solids in ~400 mL water; or of impinger liquid before dilution (sets 1 & 2)
[b] Cl^- primarily from Cl_2 by Eq. 1
[c] measured Cl^- after reduction by thiosulfate

Table 20 Distribution Chlorides between Impingers

Impinger	NaCl Run Chloride (g)	Rocky Flats Run Chloride (g)	NaCl Run Chloride Rate (g/h)	Rocky Flats Run Chloride Rate (g/h)
Set #1 Sampling Duration (h)	4.7	4.3		
Set #2 Sampling Duration (h)	2.0	2.3		
Water + Acid Set #1	11.0	11.2	2.3	2.6
Water + Acid Set #2	16.1	14.3	8.0	6.2
Base * Set #1	0.85	0.85	0.18	0.20
Base Set #2	1.31	1.20	0.66	0.52

* does not include contribution from Cl_2

The chloride data for the base impingers indicates that these impingers may have collected HCl that passed through the water and acid impingers. In general, the acid impingers collected much less chloride than expected, given the amount seen in the base impingers. However, an alternative explanation would be that there really was little HCl entering the basic impingers and that the chloride found was due to the dissolution of Cl_2 to form HCl and HClO:

$$Cl_2 + H_2O \qquad H^+ + Cl^- + HClO \qquad \text{Eq. 1}$$

It has been calculated that the amount of sodium thiosulfate used to react with Cl_2 in the basic impingers may have been significantly lower than needed. These samples will be rerun to determine if this is true and the results documented in a future report. The data in Table 18 indicate about 3.3 mmol of Cl^- from Cl_2 were found, but the amount of Cl^- from Cl_2 may have been as high as 33.4 mmol. With this hypothesis, the amounts of NaCl, NaF, HCl, HF, and Cl_2 collected are summarized in Table 21. The several reactions of NaCl and KCl are summarized in Figure 12. Either salt can decompose to form Na_2O in the glass, NaCl in the offgas particulate, and HCl or Cl_2 in the offgas.

Table 21 Estimated Alkali & Halide Content of Offgas from the Rocky Flats Run

(mmol)	NaCl	KCl	NaF	HCl	HF	Cl_2
Particulate	91.0	157.	1.88	4.58	[1]	
Acid Scrubbed	1.51	1.33	[2]	401.	26.7	
Base Scrubbed						33.4 [3]

[1] all F assumed to be NaF; some could be HF with less HCl, more NaCl
[2] all F assumed to be HF; some could be NaF with less NaCl, more HCl
[3] value estimated from chemistry of Eq. 1

$$\text{NaCl (or KCl)} \longrightarrow Na_2O + \text{Cl in glass}$$
$$\longrightarrow \text{NaCl in offgas particulate}$$
$$\longrightarrow Cl_2 \text{ in offgas}$$
$$\xrightarrow{+H_2O} \text{HCl in offgas}$$

Figure 12 Reactions of NaCl or KCl in Melter

An optical photograph of the offgas particulate collected on a filter from the Rocky Flats Run is shown in Figure 13. The particulate was off-white, very fine textured, and was easily broken up. When the particulate, which was mostly NaCl and KCl, was recovered by washing with water, the particulate balled-up into dark brown globs. When diluted with excess water, the liquid contained gelatinous brownish solids. For analysis for total metals, the laboratory dissolved these suspended solids with a few drops of concentrated nitric acid.

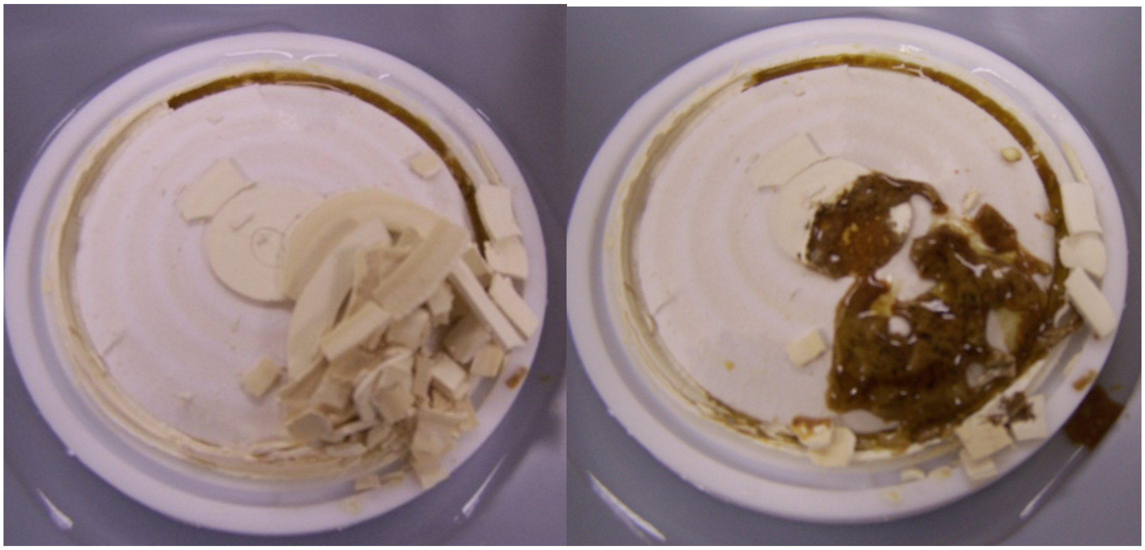


Figure 13 Photographs of Particulate on Filter from the Rocky Flats Run

Offgas particulate collected on the filter from the NaCl Run was also examined by SEM/EDS. These photographs are shown in Figure 14 through Figure 16. Photo 4 in Figure 14 shows a large particle that is similar to one (spot 3) shown in Figure 16 that was identified by EDS as a glass or frit particle; the EDS spectrum of spot 3 is shown in Figure 17. Photos 8, 9, and 10 show that there were some larger (~2 μm) agglomerated particles and cubic particles that suggest entrained NaCl. Almost all of the particles are spherical. As seen in photos 10 and 11, the salt particles were as small as 0.2 μm and that they were agglomerated. It appears that a median size may be around 0.5 μm. Spots 1 and 2 on Photo 2 were also analyzed by EDS, and these results are shown in Figure 17. Spot 1 was a frit or glass particle. Spot 2 was the bulk particulate and was identified as NaCl.

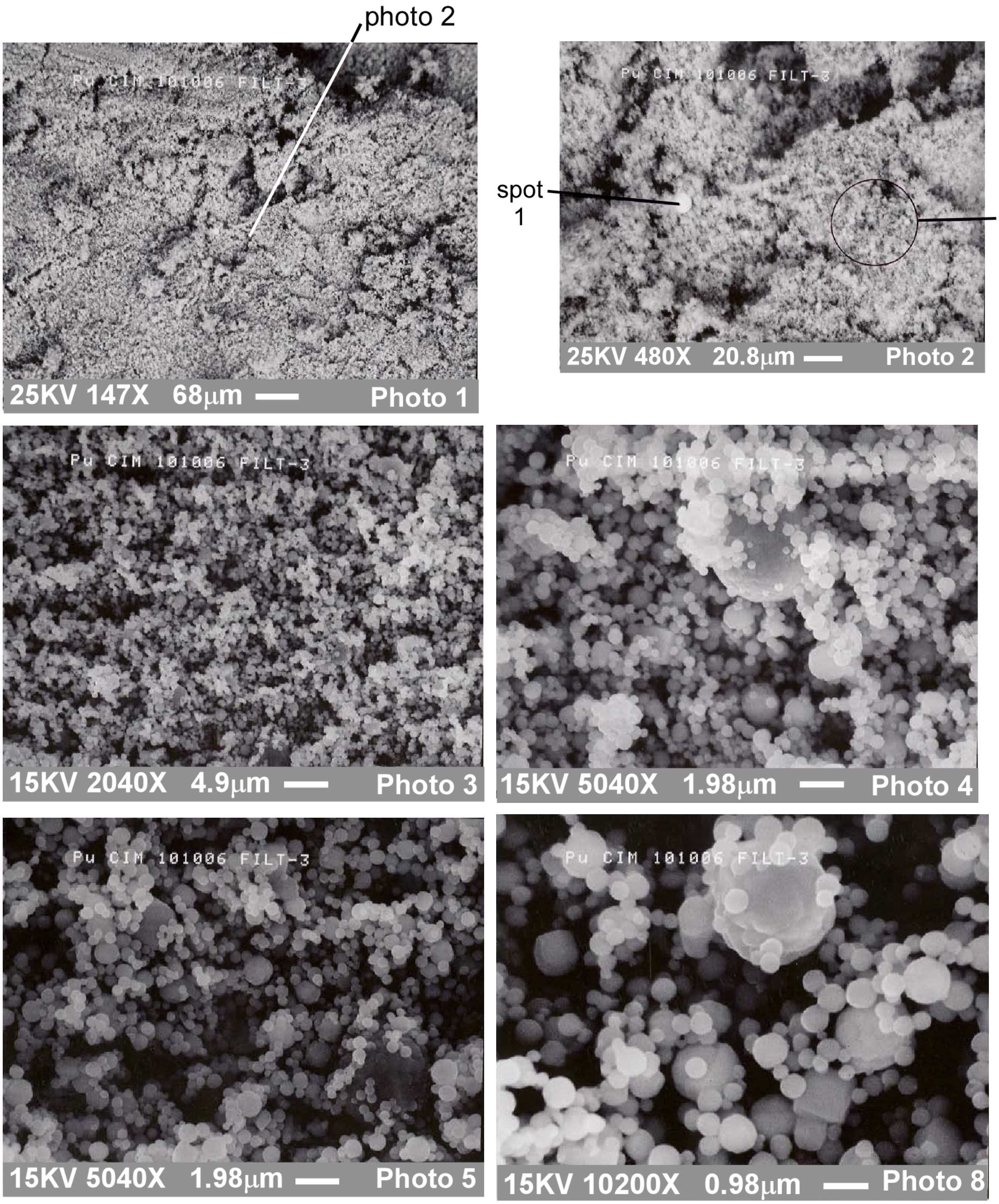


Figure 14 SEM Photographs 1-5, 8 of Offgas Particulate from the NaCl Run

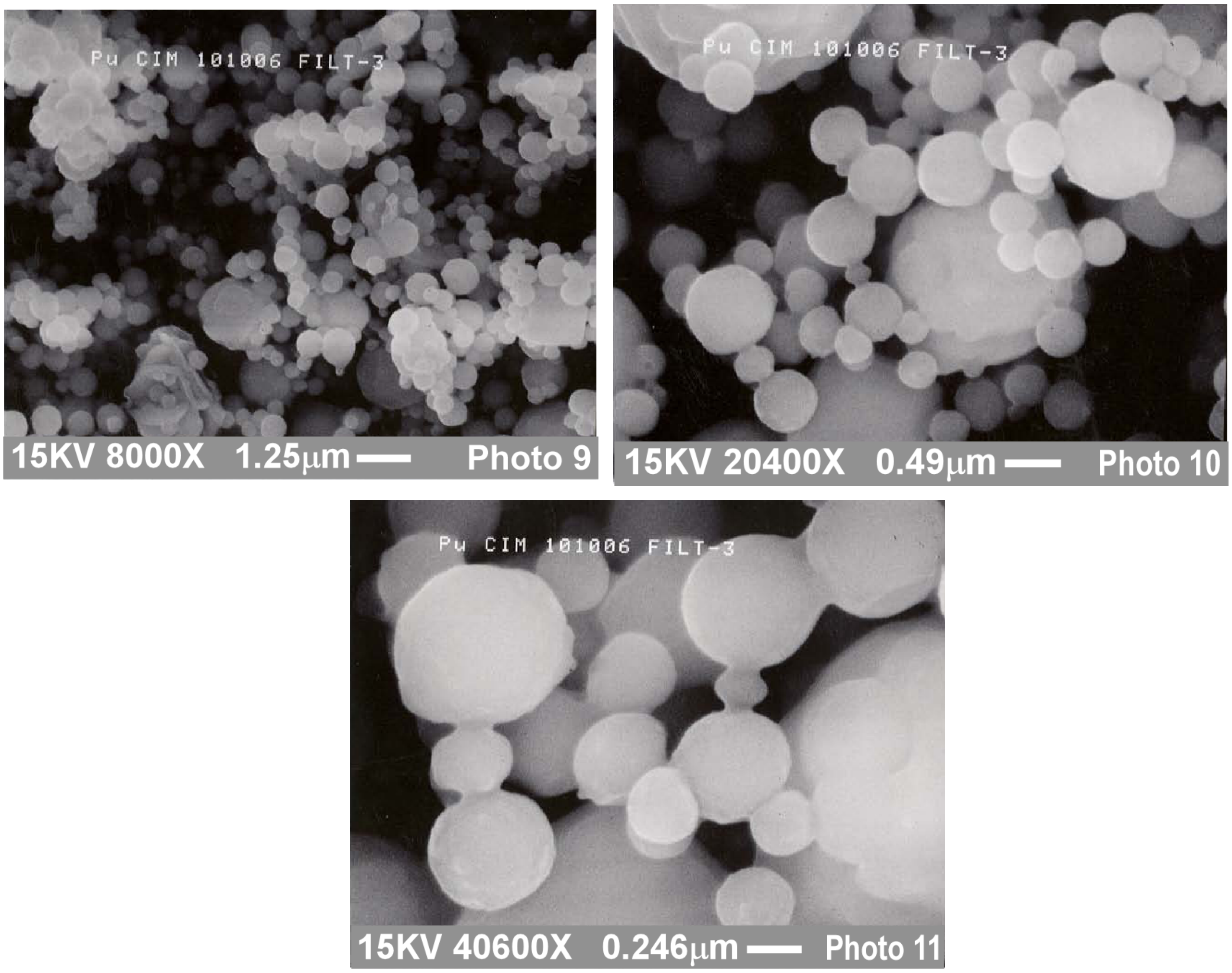


Figure 15 SEM Photographs 9-11 of Offgas Particulate from the NaCl Run

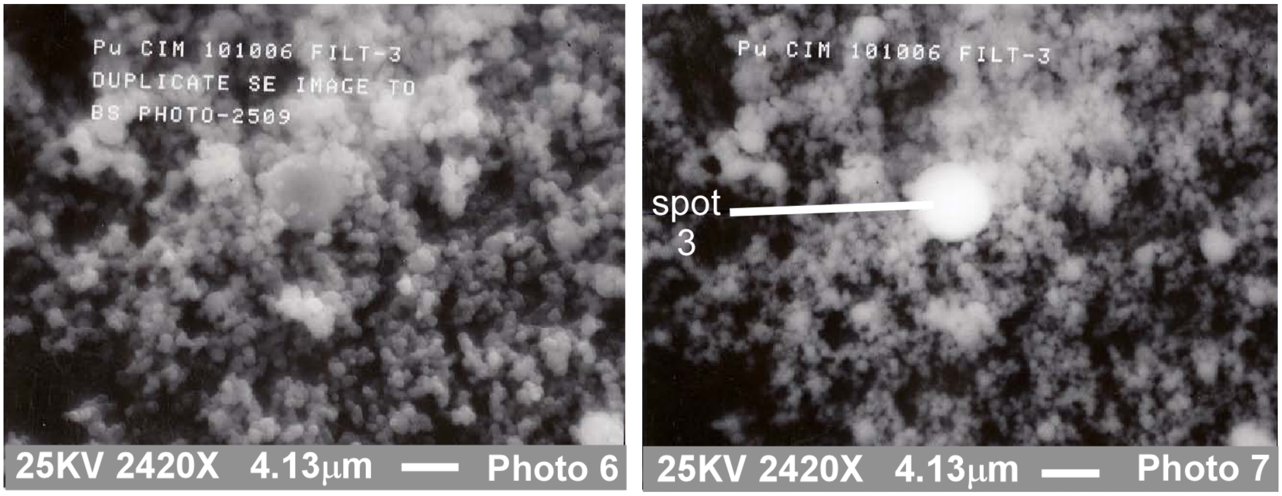
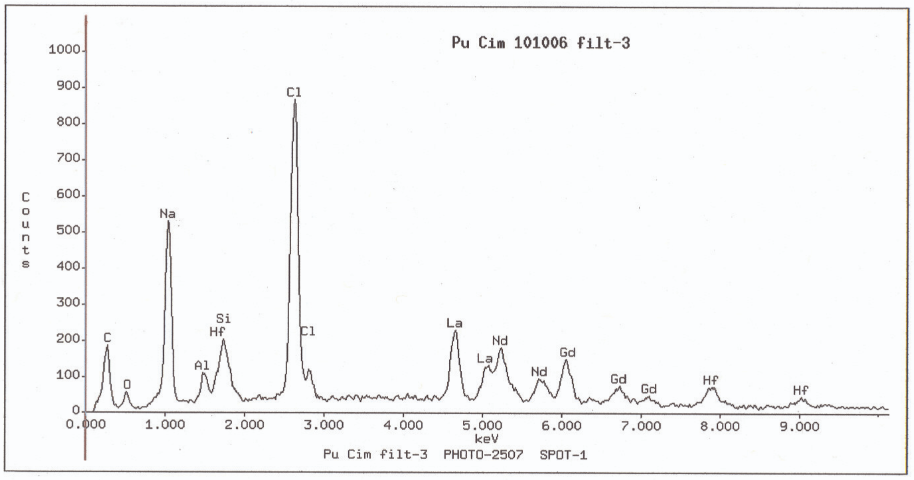
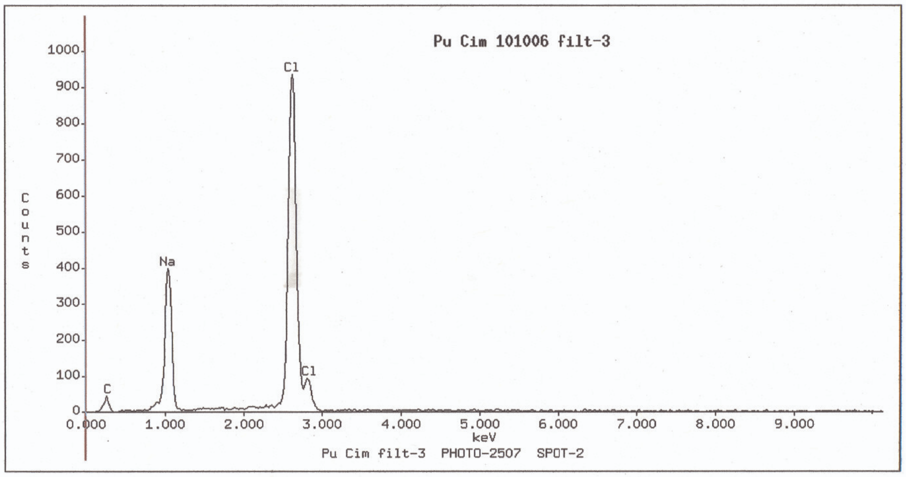


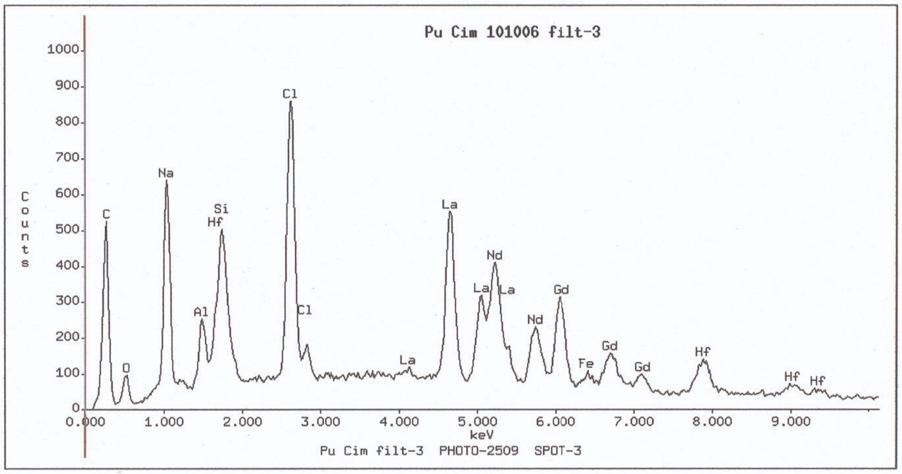
Figure 16 SEM Photographs 6-7 of Offgas Particulate from the NaCl Run



Pu Cim filt-3 PHOTO-2507 SPOT-1



Pu Cim filt-3 PHOTO-2507 SPOT-2



Pu Cim filt-3 PHOTO-2509 SPOT-3

Figure 17 EDS Spectra of Offgas Particulate Samples

The quartz offgas line was removed after each run and examined. After the NaCl Run, the inside of the line was coated with a small amount of a brown glassy solid and the top edge was covered with a small amount of gray particulate solids. In the Rocky Flats Run, there was a buildup of reddish brown crystals inside the offgas line and the top edge was again covered with gray particulate solids. A photo of the offgas line from the Rocky Flats Run is shown in Figure 18. The total mass of the crystals recovered was only about 0.05 g.

Figure 18 Offgas Line from the Rocky Flats Run Showing Crystalline Buildup and Deposits

The crystalline deposits were analyzed by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) and were also dissolved and analyzed by ICP-AES for elements. The quartz offgas line minus the crystals removed was analyzed by ICP-AES after dissolving much, but not all of the solids deposits in aqua regia. The XRD of the crystals is shown in Figure 19. The crystals were identified as a mixture of KCl, NiO, and what appears to be a solid solution of metal borates with a ludwigite-like structure such as bonaccordite $(Ni_2)^{+4}(Fe)^{+3}(BO_5)^{-7}$. Bonaccordite is a reddish brown crystal.

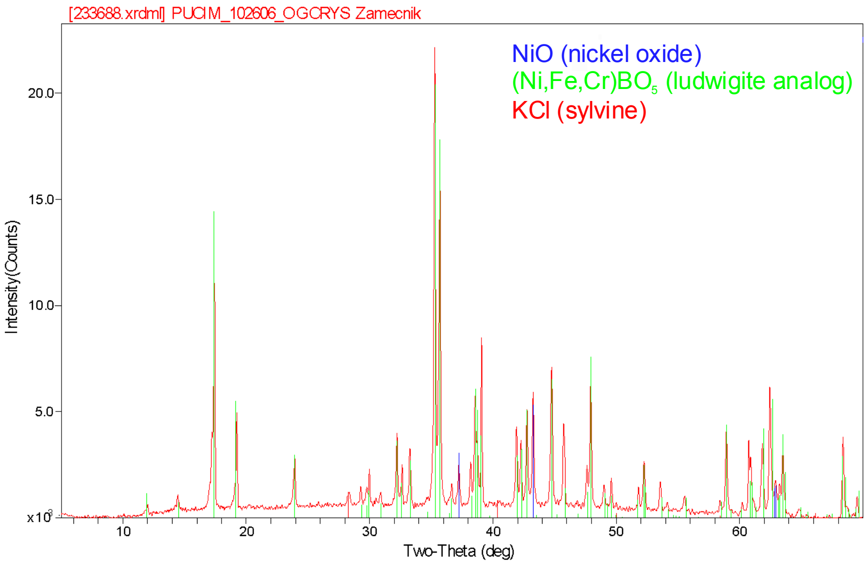


Figure 19 XRD Spectrum of Offgas Crystal Deposits

The composition of the crystal deposits and the deposits dissolved from the offgas line are shown in Table 22. In both the crystals and the deposits, boron predominated on a molar basis by 2:1 over the combined Na + K, which were the next most abundant. Because KCl was identified by XRD it is also likely that NaCl was present. To account for the significant amount of boron found, the presence of alkali borates (NaB_3O_5, $NaBO_2$, $Na_2B_4O_7$) is also likely. Iron and nickel were the next most abundant, in accord with the presence of bonaccordite. The transition metals Mo and W and also Sr were next in abundance, followed by Cr and Cu. Small amounts of the lanthanides, Hf, Al, and Si were also found. These would be accounted for by entrainment of glass or frit. Si will also be present from dissolution of some of the quartz.

Table 22 Composition of Offgas Crystals and Offgas Deposits from the Rocky Flats Run

	--------Crystals--------		**------Deposits------**	
Element	**mg/kg**	**mmol/kg crystals**	**mg/kg**	**mmol/kg offgas line**
Al	820	30.4	1055	39.1
B	**44900**	**4153**	**119000**	**11007**
Ca	<10	NA	<10	NA
Cr	440	8.46	1650	31.7
Cu	330	5.19	1445	22.7
Fe	*3525*	*63.1*	*11600*	*208*
Gd	220	1.40	136	0.87
Hf	103	0.57	59	0.33
K	**25450**	**651**	**189000**	**4834**
La	220	1.58	208	1.49
Mg	<10	NA	152	6.25
Mo	1490	15.5	2095	21.8
Na	**38900**	**1692**	**129000**	**5611**
Nd	368	2.55	180	1.25
Ni	*3075*	*52.4*	*8460*	*144*
P	<1000	NA	<1000	NA
Pb	<10	NA	<10	NA
S	<500	NA	<500	NA
Si *	3355	119	22300	794
Sr	2140	24.4	2525	28.8
W	2175	11.8	829	4.51
Zr	<10	NA	449	4.92

bold: most abundant *italic: most abundant metals*
shaded: frit components * Si present in quartz offgas line

3.2 Glass Composition

The predicted and measured glass compositions for the NaCl and Rocky Flats Runs are shown in Table 23. The table gives the composition predicted from subtracting the measured offgas species from the feed. Elements that deviated more than 25% from the predicted composition are shown in bold in the % Difference column.

For the NaCl Run, all species except Cl were within 25% of the predicted concentrations. The measured chloride in the glass was lower than predicted because the measured total chloride in the offgas was probably lower than the actual amount in the offgas. Small amounts of Ca, Cu, Fe, and Zr were found in the the NaCl Run glass even though none was intentionally added in the Frit X, HfO_2, or impurity NaCl. In the Rocky Flats Run, the Ca, Cu, Fe, and Zr were again higher than the amounts added to the feed; in fact, the Ca, Cu and Fe present as impurities were higher than the intended amount to be added. The source of Zr is most likely the HfO_2 used as the surrogate for PuO_2 and for the frit; ZrO_2 is an impurity at up to 1.5 wt% in HfO_2. As mentioned previously, the source of Fe is probably processing in ferrous metal equipment, while the Cu could have come from frit screening on brass sieves. Brass contains both Cu and Zn, but Zn would not be found in the glass due to its volatility. Reanalysis of the Frit X for impurities is pending.

The Na was also higher than predicted, but only by 27.5%. Na was definitely found in the offgas as NaCl, so the total amount of Na added may have also been higher than intended. Both Ni and Cr were low; both were found to be volatile and were found in both the offgas particulate samples and in offgas line deposits. The amounts of each of these in the offgas line deposits were not accounted for in the material balance; these deposits may account for the missing Cr and Ni. The balance on chloride was good, with both the measured and predicted concentration in the glass being about 0.4 wt%.

Fluoride and chloride were measured in the glass using a sodium peroxide/sodium hydroxide fusion with water uptake that does not dissolve all of the fused product. It appears that fluoride does not dissolve in the water uptake. For test glasses made with CaF_2, the calcium was present at a molar ratio of Ca:F of 1:2 and much less than expected fluoride was found in the glass. Analysis of glasses with fluoride in significant excess over calcium give slightly low fluoride measurements. If the fluoride is bound to the calcium in the fusion, the water uptake is not likely to dissolve it, resulting in low measurements of fluoride. Analytical method development will be required to accurately quantify fluoride in the presence of excess calcium.

Table 23 Predicted and Measured Compositions of Glasses Produced from Runs the NaCl and Rocky Flats Runs.

	NaCl Run			**Rocky Flats Run**		
	Predicted From (Feed – Offgas) (wt%)	**Measured (mean of 2) (wt%)**	**% Difference (Meas.-Calc.)**	**Predicted From (Feed – Offgas) (wt%)**	**Measured (mean of 2) (wt%)**	**% Difference (Meas.-Calc.)**
Al	5.58	5.49	-1.69	5.70	5.61	-1.56
B	3.53	3.54	0.27	3.60	3.67	1.88
Ca		0.090	NA	0.044	0.213	**79.5**
Cr		<0.01	NA	0.122	0.092	**-32.0**
Cu		0.031	NA	0	0.048	**92.8**
Fe		0.049	NA	0.068	0.088	22.9
Gd	10.49	10.65	1.52	10.71	10.65	-0.55
Hf	11.39	11.20	-1.7	9.49	9.56	0.74
K		<0.1	NA	0.268	0.289	7.34
La	14.56	14.75	1.31	14.86	14.70	-1.10
Mg		<0.01	NA	0.146	0.117	-24.7
Mn		<0.01	NA	0	<0.01	NA
Mo		<0.01	NA	0.010	0.012	11.7
Na	0.730	0.724	-0.8	0.276	0.381	**27.5**
Nd	11.08	11.30	1.98	11.31	11.40	0.81
Ni		<0.01	NA	0.095	0.065	**-46.2**
P		<0.1	NA	0.0045	<0.1	NA
Si	8.80	8.93	1.44	8.99	9.10	1.28
Sr	1.87	1.88	0.41	1.91	1.89	-1.21
W		<0.1	NA	0.039	<0.1	NA
Zr		0.025	NA	0	0.045	NA
Cl	0.543	0.293	**-85.7**	0.431	0.374	-15.1
F		<0.02	NA	0.090	NA	NA
TOTAL	**68.57**	**68.95**	**0.55**	**68.16**	**68.31**	**0.21**

Table 24 shows the predicted composition of the Rocky Flats Run glass assuming incorporation into the glass of 1) all impurities; 2) only the cation (metal impurities) plus phosphorus; 3) no impurities; and 4) impurities predicted by the material balance (feed – offgas); these values are compared to the measured values. This comparison is presented on both elemental and oxide bases.

Table 24 Elemental and Oxide Concentrations Predicted and Measured for Glass from the Rocky Flats Run

Element	All Impurities (wt%)	Cation Impurities + P (wt%)	No Impurities (wt%)	Feed – Offgas (wt%)	Measured Mean (wt%)	Oxide	All Impurities (wt%)	Cation Impurities + P (wt%)	No Impurities (wt%)	Feed – Offgas (wt%)	Measured Mean (wt%)
Al	5.63	5.70	5.81	5.70	5.61	**Al_2O_3**	10.63	10.78	10.99	10.77	10.60
B	3.56	3.61	3.68	3.60	3.67	**B_2O_3**	11.47	11.63	11.85	11.60	11.83
Ca	0.043	0.044	0	0.044	0.213	**CaO**	0.060	0.061	0	0.061	0.298
Cr	0.125	0.126	0	0.122	0.092	**Cr_2O_3**	0.182	0.184	0	0.178	0.135
Cu	0.008	0.008	0	0.003	0.048	**CuO**	0.010	0.010	0	0.004	0.060
Fe	0.070	0.071	0	0.068	0.088	**Fe_2O_3**	0.099	0.101	0	0.097	0.126
Gd	10.57	10.72	10.92	10.71	10.65	**Gd_2O_3**	12.18	12.35	12.59	12.34	12.28
Hf	9.38	9.51	9.69	9.49	9.56	**HfO_2**	11.06	11.21	11.43	11.19	11.27
K	0.471	0.477	0	0.268	0.289	**K_2O**	0.567	0.575	0	0.323	0.348
La	14.67	14.87	15.16	14.86	14.70	**La_2O_3**	17.21	17.44	17.78	17.43	17.24
Mg	0.144	0.146	0	0.146	0.117	**MgO**	0.239	0.243	0	0.242	0.194
Mo	0.014	0.014	0	0.010	0.012	**MoO_3**	0.020	0.021	0	0.016	0.018
Na	0.345	0.350	0	0.276	0.381	**Na_2O**	0.465	0.472	0	0.373	0.514
Nd	11.16	11.32	11.53	11.31	11.40	**Nd_2O_3**	13.02	13.20	13.45	13.19	13.30
Ni	0.117	0.119	0	0.095	0.065	**NiO**	0.149	0.151	0	0.121	0.082
P	0.004	0.004	0	0.004	<0.1	**P_2O_5**	0.010	0.010	0	0.010	<
Si	8.87	8.99	9.17	8.99	9.10	**SiO_2**	18.98	19.24	19.61	19.22	19.47
Sr	1.89	1.91	1.95	1.91	1.89	**SrO**	2.23	2.26	2.30	2.26	2.23
W	0.039	0.040	0	0.039	<0.1	**WO_3**	0.050	0.050	0	0.050	<
Zr	0	0	0	0	0.045	**ZrO_2**	0	0	0	0	0.061
Cl	1.25	0	0	0.431	0.374	**Cl**	1.25	0	0	0.431	0.374
F	0.107	0	0	0.090	NA	**F**	0.107	0	0	0.090	<
TOTAL	**68.47**	**68.04**	**67.92**	**68.16**	**68.31**	**TOTAL**	**100**	**100**	**100**	**100**	**100.43**

< alone indicates element measured value was below detection limit

The glass compositions on an elemental and an oxide basis for the NaCl and Rocky Flats Runs are compared in Table 25. The oxide totals for both were very close to the expected 100%. The Hf content of the NaCl Run glass was higher than the Rocky Flats Run glass as expected due to a higher target value. XRD measurements on the glass from the NaCl Run showed a small amount of crystalline HfO_2 present.

Table 25 Measured Compositions of Glass from the NaCl and Rocky Flats Runs

		NaCl Run				**Rocky Flats Run**			
Element	**Oxide**	**Sample 1 (wt%)**	**Sample 2 (wt%)**	**Mean**	**Oxides (wt%)**	**Sample 1 (wt%)**	**Sample 2 (wt%)**	**Mean**	**Oxides (wt%)**
Al	Al_2O_3	5.52	5.47	5.49	10.37	5.56	5.67	5.61	10.60
B	B_2O_3	3.54	3.54	3.54	11.40	3.64	3.71	3.67	11.83
Ca	CaO	0.103	0.078	0.090	0.126	0.195	0.231	0.213	0.298
Cr	Cr_2O_3	<0.01	<0.01	<0.01	0	0.093	0.092	0.092	0.135
Cu	CuO	0.031	0.032	0.031	0.039	0.056	0.040	0.048	0.060
Fe	Fe_2O_3	0.052	0.047	0.049	0.070	0.086	0.091	0.088	0.126
Gd	Gd_2O_3	10.65	10.65	10.65	12.28	10.80	10.50	10.65	12.28
Hf	HfO_2	11.10	11.30	11.20	13.21	9.56	9.56	9.56	11.30
K	K_2O	<0.1	<0.1	<0.1	0	0.282	0.296	0.289	0.348
La	La_2O_3	14.75	14.75	14.75	17.30	14.95	14.45	14.70	17.24
Mg	MgO	<0.01	<0.01	<0.01	0	0.110	0.125	0.117	0.194
Mo	MoO_3	<0.01	<0.01	<0.01	0	0.012	0.012	0.012	0.018
Na	Na_2O	0.723	0.725	0.724	0.976	0.427	0.336	0.381	0.514
Nd	Nd_2O_3	11.35	11.25	11.30	13.18	11.35	11.45	11.40	13.30
Ni	NiO	<0.01	<0.01	<0.01	0	0.060	0.070	0.065	0.082
P	P_2O_5	<0.1	<0.1	<0.1	0	<0.1	<0.1	<0.1	0
Si	SiO_2	8.96	8.90	8.93	19.10	9.03	9.18	9.10	19.47
Sr	SrO	1.88	1.88	1.88	2.22	1.92	1.86	1.89	2.23
W	WO_3	<0.1	<0.1	<0.1	0	<0.1	<0.1	<0.1	0
Zr	ZrO_2	0.025	0.025	0.025	0.034	0.069	0.021	0.045	0.061
Cl	Cl	0.294	0.291	0.293	0.293	0.370	0.379	0.374	0.374
F *	F	<0.02	<0.02	<0.02	0	<0.02	<0.02	NA	0
	TOTAL				100.6				100.4

* measured; based on material balance (feed & offgas), estimate F in glass to be ~0.09 wt%

4.0 SUMMARY & CONCLUSIONS

The following summarizes the results of these tests and conclusions that can be drawn.

- Approximately 72% of NaCl added as an impurity at 2.5 wt% in the feed was emitted into the offgas as particulate NaCl, HCl, or Cl_2.
- About 54-61% of an impurity mixture added at 3.16 wt% in the feed was emitted into the offgas as particulate or vapor.
- Particulate generated was mostly NaCl and KCl (these were the major impurities added).
- Offgas vapors consisted of HCl, Cl_2, and HF. HCl and Cl_2 could not be totally distinguished.
- Feed entrainment as indicated by frit elements in the offgas particulate was <0.03 wt% except for Sr (<0.1 wt%), B (0.13-0.16 wt%), and Hf (0.16 wt%). Sr and B are the most volatile components of the frit. HfO_2 surrogate may have been entrained.

- About 65% of the Cl, 20-25% of the Na, and 45% of the K fed were evolved into the offgas system.
- The elements Cu, Mo, Ni, Fe, and Cr were also volatile (60, 25, 20, 4, 3%, respectively).
- Crystalline deposits found in the offgas line consisted of KCl, NiO, and Ni_2FeBO_5 and similar compounds with Cr.
- About 83% of F fed, or 0.09 wt% in glass, was retained in the glass (by material balance; F at this concentration could not be quantified directly).
- Chloride (Cl) in the glass ranged from 0.29-0.37 wt%.
- Particulate consisted of water insoluble Al, Fe, Mo, W, PO_4^{-3}, partially soluble F, Cr, K, and soluble Cl, B, Cu, Ni, Na, Sr.
- Approximately 99.2 wt% of volatilized species (excluding HCl, Cl_2, HF) were collected on the nominal 0.3 μm filter.
- Visible particulate was evolved 1) from the impurity mixture at 680 °C, 2) from NaCl only at 980 °C, and 3) from the remelt of the impurity mixture at 1170 °C (indicating salt impurities were trapped within the glass matrix).
- Particulate emission rates were 0.8-2.6 g/kg glass/h.
- Particulate generated was mostly spherical salt particles as small as 0.2 μm, with an approximate median size of about 0.5 μm. Larger agglomerates may have also been present.
- Particulate particles stick together by forming bridges between them when caught on the filter.
- NaCl forms Na_2O and Cl in the glass, NaCl particulate, and HCl + Cl_2 gas. (KCl behaves similarly.)
- Fluorides are retained in the glass (F) and also emitted to the offgas as salts (e.g., NaF, KF) and HF gas.
- Melter runs with LaBS Frit X exhibited consistent behavior allowing repeatable temperature profiles for offgas testing.
- Use of batch chemicals including boric acid for frit production required additional soak time at low power to avoid bed expansion.
- Pouring behavior was consistent and yielded complete discharge of glass from the melter while leaving a sufficient plug in the drain tube for the following run.

5.0 RECOMMENDATIONS

1. Measure the aerodynamic particle size distribution of the offgas particulate with a cascade impactor.

2. Perform offgas characterization tests with all compounds that could be washed out with water removed (e.g., NaCl, KCl).

3. Test salt feed concentrations near their apparent “solubility limit” in the glass (e.g. ~0.3 wt % Cl)

4. Test simple impingement devices for collection of particulate salts from the offgas.

5. Determine if the bubbler is required for thorough mixing to be achieved in the CIM.

6. Measure the particle size distribution of the HfO_2 used.

7. Add additional thiosulfate reductant and repeat measurements of chloride in offgas samples where incomplete conversion of Cl_2 to Cl^- is suspected.

6.0 REFERENCES

[1] T.M. Jones, J.C. Marra, D.M. Immel and B.Z. Meers, *Glass Macrocracking Determination in Prototypic Canisters Containing Lanthanide Borosilicate Glass*, **WSRC-TR-2006-00015**, January 2006.

[2] J.C. Marra, D.K. Peeler, and C.M. Jantzen, *Development of an Alternative Glass Formulation for Vitrification of Excess Plutonium*, **WSRC-TR-2006-00031**, January 2006.

[3] T.M. Jones, *Americium-Curium Stabilization – 5" Cylindrical Induction Melter System Design Basis (U)*, **SRT-AMC-99-0001**, January 1999.

[4] T.M. Jones, D.H. Miller, J.W. Duval, R.F. Schumacher and J.M. Marra, *ITS Research and Development – ACTL CIM5 Operation Laboratory Notebook*, **WSRC-NB-2001-00086**, July 2005 – October 2006.

[5] T.M. Jones and D.H. Miller, *Pu Immobilization Program CIM Testing Laboratory Notebook*, **WSRC-NB-2006-00144**, November 2006.

[6] J.R. Zamecnik, S. Jung, *Analysis of Characterization Data for Surrogate Plutonium Glasses with Impurities*, **M&O-PUD-2006-00067, Rev. 0**.

[7] D.T. Herman, *Trip Report from Travel to Union Process*, **M&O-PUD-2006-00094.**

[8] *(EPA) Method 26 - Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Non-Isokinetic Method*, **40 CFR 60 Appendix A**.

[9] *Job Hazards Analysis*, **SRNL-PSE-2006-00232**.

[10] *Environmental Evaluation Checklist*, **TC-W-2006-104**.

[11] J.M. Tingey and S.A. Jones, *Chemical and Radiochemical Composition of Thermally Stabilized Plutonium Oxide from the Plutonium Finishing Plant Considered as Alternate Feedstock for the Mixed Oxide Fuel Fabrication Facility*, **PNNL-15421**, July 2005.

[12] J.R. Zamecnik and V.J. Williams, *Plutonium Vitrification Testing Laboratory Notebook*, **WSRC-NB-2006-00030**, October – November 2006.

7.0 APPENDIX

Table 26 9/05/06 Run Data (1/10th Data Shown)

Minutes	Glass Temp deg C	Melter Top T2 deg C	Melter Midpoint T3 deg C	Control T4 deg C	Cyl Bottom T5 deg C	Cone Midpoint T6 deg C	Cone Midpoint T7 deg C	Drain Top T8 deg C	XP20 volts	XP20 amps	XP20 KVA	XP20 KHz	XP5 volts	XP5 amps	XP5 KVA	XP5 KHz
1	19	18	17	21	20	18	17	17	35	2	0.07	350	2	0	0	0
10	27	81	105	103	96	95	87	87	70	8	0.56	96	69	4	0	0.27
20	73	131	154	154	151	150	146	147	70	9	0.63	97	68	4	0	0.27
30	136	163	187	188	188	189	187	182	70	9	0.63	97	68	4	0	0.27
40	151	210	258	261	259	252	243	238	93	12	1.11	97	86	6	0	0.51
50	167	273	335	343	343	332	325	315	97	13	1.26	97	91	6	0	0.54
60	201	336	411	420	424	406	400	392	103	13	1.33	97	95	6	0	0.57
70	250	396	483	496	495	475	468	458	110	14	1.54	97	99	7	0	0.69
80	315	458	557	569	570	544	537	519	117	15	1.75	97	107	7	0	0.74
90	377	522	631	644	644	616	609	590	124	16	1.98	97	113	7	0	0.79
100	453	586	717	729	702	680	689	665	131	17	2.22	97	119	7	212	0.83
110	563	668	809	821	824	782	781	754	137	19	2.6	97	126	9	240	1.13
120	681	723	893	916	905	858	859	836	144	20	2.88	98	131	9	213	1.17
130	778	780	959	976	967	917	916	890	151	20	3.02	97	135	8	228	1.08
140	873	831	1013	1034	1024	972	970	940	157	22	3.45	97	139	9	235	1.25
150	959	881	1051	1076	1071	1022	1018	989	164	23	3.77	98	147	9	229	1.32
160	1048	936	1064	1102	1109	1064	1057	1029	171	24	4.1	98	153	10	252	1.53
170	1109	1013	1078	1118	1139	1103	1086	1061	177	24	4.24	98	157	11	225	1.72
180	1127	1101	1166	1151	1162	1142	1110	1082	184	26	4.78	98	163	11	237	1.79
190	1147	1165	1233	1214	1218	1189	1147	1113	190	27	5.13	98	167	11	237	1.83
200	1224	1211	1277	1254	1262	1235	1205	1180	197	28	5.51	98	170	13	225	2.21
210	1281	1264	1335	1307	1318	1282	1251	1229	203	30	6.09	98	181	12	217	2.17
220	1363	1315	1386	1352	1367	1340	1314	1298	210	31	6.51	98	187	12	240	2.24
230	1424	1359	1433	1393	1410	1389	1371	1359	216	31	6.69	98	190	13	241	2.47
240	1420	1368	1447	1405	1422	1378	1340	1328	219	32	7	98	191	13	251	2.48
250	1401	1362	1448	1404	1418	1365	1324	1310	221	32	7.07	98	191	13	251	2.48
260	1397	1361	1449	1405	1418	1362	1320	1306	223	32	7.13	98	191	13	251	2.48
270	1396	1361	1449	1404	1416	1361	1319	1304	222	32	7.1	98	191	13	251	2.48
280	1395	1360	1449	1404	1415	1360	1317	1303	223	32	7.13	98	191	13	251	2.48
290	1394	1360	1448	1403	1414	1360	1317	1302	222	32	7.1	98	191	13	251	2.48
300	1394	1360	1449	1402	1414	1359	1317	1302	223	32	7.13	98	191	13	251	2.48
310	1393	1360	1449	1402	1414	1359	1316	1301	222	32	7.1	98	191	13	251	2.48
320	1393	1360	1448	1401	1413	1359	1316	1301	223	32	7.13	98	191	13	251	2.48
330	1393	1361	1448	1401	1412	1359	1316	1300	223	32	7.13	98	191	13	251	2.48
340	1393	1360	1449	1401	1413	1359	1316	1300	223	32	7.13	98	191	13	251	2.48
350	1393	1360	1448	1400	1412	1359	1315	1300	223	32	7.13	98	191	13	251	2.48
360	1393	1360	1448	1399	1412	1359	1315	1300	222	32	7.1	98	191	13	251	2.48
370	1393	1360	1448	1399	1412	1358	1315	1299	223	32	7.13	98	191	13	251	2.48
380	1393	1360	1448	1399	1411	1358	1315	1299	223	32	7.13	98	191	13	251	2.48
390	1393	1360	1447	1399	1412	1358	1315	1299	222	32	7.1	98	191	13	251	2.48
400	1393	1360	1448	1399	1412	1358	1315	1298	222	32	7.1	98	191	13	251	2.48
410	1394	1360	1448	1399	1412	1359	1316	1301	223	32	7.13	98	191	13	251	2.48
420	1419	1369	1451	1405	1424	1377	1332	1308	223	32	7.13	98	191	13	251	2.48
430	1321	1275	1345	1303	1319	1275	1226	1211	193	28	5.4	98	191	13	251	2.48
440	1140	1103	1163	1129	1141	1099	1057	1044	159	22	3.49	98	191	13	251	2.48
450	944	915	964	937	946	909	873	862	126	18	2.26	97	191	13	251	2.48
460	125	720	753	732	737	706	678	669	93	13	1.2	97	191	13	251	2.48